

Electronic Properties of h - WO_3 and CuWO_4 Nanocrystals as Determined from X-ray Spectroscopy and First-Principles Band-Structure Calculations

V. V. Atuchin, I. B. Troitskaia, O. Yu. Khyzhun, V. L. Bekenev, and Yu. M. Solonin

Abstract—The electronic structure of hexagonal WO_3 and triclinic CuWO_4 nanocrystals, prospective materials for functional electronic devices, has been studied using the X-ray photoelectron spectroscopy (XPS) and X-ray emission spectroscopy (XES) methods. The present XPS and XES results render that the W 5d- and O 2p-like states contribute throughout the whole valence-band region of the h - WO_3 and CuWO_4 nanocrystalline materials, however maximum contributions of the O 2p-like states occur in the upper, whilst the W 5d-like states in the lower portions of the valence band, respectively. Calculations of band dispersions for several symmetry directions of CuWO_4 have been made using the first-principles self-consistent full potential linearized augmented plane wave (FP-LAPW) method. The FP-LAPW calculations render that CuWO_4 is an indirect-gap material.

Index Terms—tungstate; nanocrystal; oxide; electronic structure.

I. INTRODUCTION

Tungsten oxides are recognized among effective materials for photocatalytic water splitting with generation of hydrogen and oxygen [1]-[4]. Numerous efforts were spent to prepare WO_3 and complex tungstates crystals as nanobelts, whiskers, nanorods and nanoslabs with potentials for using in nanoarchitecture [2], [5]-[9]. Tungstate crystals and films possess interesting optical, electrochromic, gas-sensing properties and are widely used as functional elements in various device structures [10]-[13]. Complex tungstate crystals typically display a framework-type crystal structure with distorted cavities or channels stuffed with other cations at low-symmetry oxygen environment that results in noncentrosymmetric crystal structure. As a result, many tungstates show nonlinear optical properties or are suitable hosts for lasant ions [14]-[20]. Photocatalytic, optical and

electro-physical properties of tungstates are a complex function of phase composition and the electronic structure of the crystals [3], [4], [21]-[23].

Present study is aimed to consider general trends found for the electronic properties of tungsten oxide and complex tungstates. Besides this, low-temperature preparation of tungsten oxide nanocrystals with developed surface area will be proposed. General factors defined chemical stability of top surface of tungstates will be also evaluated. For such a study, nanocrystals of hexagonal tungsten trioxide (h - WO_3) and triclinic copper tungstate (CuWO_4) have been chosen.

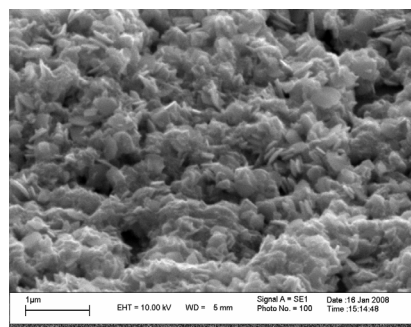


Fig. 1. SEM image of h - WO_3 nanocrystals.

II. EXPERIMENTAL

Earlier, low-temperature precipitation reaction with nitric acid from aqueous solution of the ammonium salt was developed for fabrication of well-shaped molybdenum and germanium oxide nanocrystals [24]-[28]. Layered molybdenum and tungsten oxides are the structural analogues and possess strongly anisotropic structure. In present study this reaction was tested for the formation of tungsten oxide nanocrystals. The precipitation was produced under $T = 100^\circ\text{C}$ and $pH = 1$. As it shown in Fig.1, the h - WO_3 nanoplates with 10 nm thick and 100 nm diameter were produced. Phase composition of the final product was confirmed with XRD analysis and Raman spectroscopy [29]. The DTA curve recorded up to $T = 500^\circ\text{C}$ in air shows the thermal transformation of hexagonal h - WO_3 to monoclinic β - WO_3 at $T_f = 390$ - 400°C . Most intensive Raman lines at 967, 685, 223 and 122 cm^{-1} are attributed to the bridged O-W-O bonding.

A comparative experimental study of the electronic structure of h - WO_3 and CuWO_4 nanocrystals has been made using the XPS and XES methods. Details of sample preparation and of experimental techniques can be found elsewhere [21], [22], [30]-[34].

Manuscript received May 12, 2011; revised June 15, 2011.

V. V. Atuchin is with the Laboratory of Optical Materials and Structures, Institute of Semiconductor Physics, SB RAS, Novosibirsk, 630090, Russia (e-mail: atuchin@thermo.isp.nsc.ru).

I. B. Troitskaia is with the Laboratory of Optical Materials and Structures, Institute of Semiconductor Physics, SB RAS, Novosibirsk, 630090, Russia (e-mail: troitskaia@thermo.isp.nsc.ru).

O. Yu. Khyzhun is with Frantsevich Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, Kiev, UA-03142, Ukraine (e-mail: khyzhun@ipms.kiev.ua).

V. L. Bekenev is with Frantsevich Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, Kiev, UA-03142, Ukraine (e-mail: bekenev@ipms.kiev.ua).

Yu. M. Solonin is with Frantsevich Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, Kiev, UA-03142, Ukraine (e-mail: solonin@ipms.kiev.ua).

III. COMPUTATIONAL DETAILS

Calculations of band dispersions for several symmetry directions of CuWO_4 have been made using the first-principles self-consistent full potential linearized augmented plane wave (FP-LAPW) method with the WIEN97 code [35]. Like in the calculations of total and partial densities of states of copper tungstate [33], in the present FP-LAPW calculations, lattice parameters and positions of the constituent atoms of CuWO_4 have been chosen in accordance with the crystallography data determined for the compound by Kihlborg and Gebert [36]. Crystal structure of CuWO_4 is shown in Fig. 2.

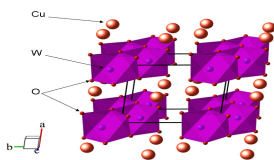


Fig. 2. Crystal structure of CuWO_4 . Unit cell is outline. Oxygen lone atoms are omitted for clarity.

The generalized gradient approximation (GGA) by Perdew et al. [37] have been used for calculations of the exchange-correlation potential. The *muffin-tin* (MT) sphere radii of the constituent atoms of CuWO_4 in the present calculations were assumed to be 0.873 Å for W and O and 1.005 Å for Cu. The $R_{\min}^{MT} k_{\max}$ parameter, where R_{\min}^{MT} denotes the smallest MT sphere radius and k_{\max} determines the value of the largest k vector in the plane wave expansion, were assumed to be 10.0 (the charge density was Fourier expanded up to the value $G_{\max} = 14$). In the potential decomposition, the valence wavefunctions inside the MT spheres were expanded up to $l_{\max} = 3$. The basis function of the atomic orbitals of Cu, W, and O was analogous to that employed in [28]. Integration through the Brillouin zone was carried out using the tetrahedron method by Blöchl et al. [38]. The Brillouin zone sampling has been done using 92 k -points within the irreducible part of the zone. The iteration process was checked taking into account the changes of total energy and the calculations were interrupted when for three following iterations the change of total energy was less than $\sim 1 \times 10^{-5}$ eV. Calculations of band dispersions for several symmetry directions of $h\text{-WO}_3$ are in progress by our group.

IV. RESULTS AND DISCUSSION

Results of comparison on a common energy scale of the experimental X-ray emission $\text{W L}\beta_5$ and $\text{O K}\alpha$ bands, representing the energy distributions of the W 5d- and O 2p-like states, respectively, for the $h\text{-WO}_3$ and CuWO_4 nanocrystals under study are presented in Figs. 3 and 4. In these figures, for comparison, the XPS valence-band spectrum (excited by $\text{Mg K}\alpha$ radiation) of the corresponding compound is also presented. The method of matching the X-ray emission bands on a common energy scale was analogous to that applied successfully when studying the electronic structure of transition metal oxides and tungstates [21], [31].

Data of matching the X-ray emission bands on a common energy scale (Figs. 3 and 4) render that, for the $h\text{-WO}_3$ and

CuWO_4 nanocrystals under consideration, the main contributions of the W 5d- and O 2p-like states are observed at the bottom and near the top of the valence band, respectively, with contributions of the mentioned states throughout other portions of the valence band of the compounds. The above experimental results confirm the data of the first-principles FP-LAPW calculations of copper tungstate [33].

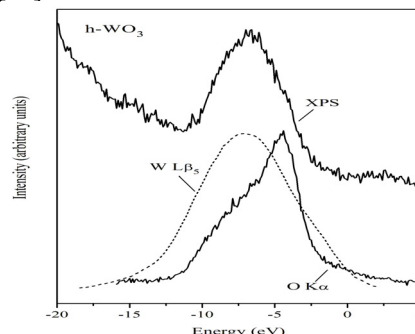


Fig. 3. The X-ray emission $\text{W L}\beta_5$ and $\text{O K}\alpha$ bands matched on a common energy scale with the XPS valence-band spectrum of $h\text{-WO}_3$ nanocrystals.

Predominant contributions of the W 5d- and O 2p-like states into the lower and upper portions of the valence band, respectively, established for $h\text{-WO}_3$ and CuWO_4 , look to be a common peculiarity of the electronic structure of tungsten trioxide and MWO_4 tungstates. In particular, this peculiarity was either experimentally or theoretically detected for a number of MWO_4 ($M = \text{Fe, Co, Pb, Cd, Zn, Sr}$) compounds [39]-[41]. However, main contributions of the valence states associated with the M atom depend significantly on its position in the Periodic Table. Partly, the theoretical band-structure calculations [33] have revealed that the top of the valence band of CuWO_4 is dominated by contributions of Cu 3d-like states. However, Cu states do not contribute significantly into the conduction band of the compound [33]. Additionally, Zhang et al. [40] have established minor contributions of lead atoms into the total density of states (DOS) within the energy region corresponding to the positions of the valence and conduction bands of PbWO_4 . Nevertheless, in CaWO_4 , calcium atoms contribute dominantly into the upper portion of the conduction band (at energies higher than 7 eV above the top of the valence band of the tungstate [40]). It is worth mentioning that contributions of cadmium atoms dominate the bottom of the valence band of CdWO_4 tungstate, however no significant Cd contributions throughout the conduction band of the compound were detected in calculations by Abraham et al. [41].

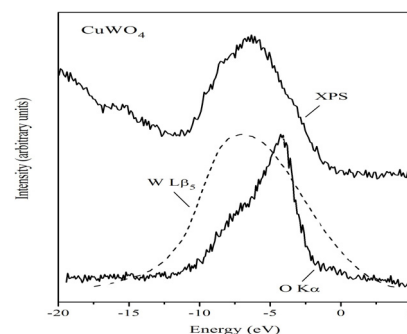


Fig. 4. The X-ray emission $\text{W L}\beta_5$ and $\text{O K}\alpha$ bands matched on a common energy scale with the XPS valence-band spectrum of CuWO_4 nanocrystals.

Band dispersions for CuWO_4 are plotted in Fig. 5 for several symmetry directions of the triclinic Brillouin zone (Fig. 6), which is characteristic of the compound under consideration. It is worth mentioning that Fig. 6 was plotted adopting the program [42], and in this figure the coordinates of the k -points, within the limited region of the Brillouin zone studied for the band dispersions shown in Fig. 5, are as follows: Γ (0.0 0.0 0.0), X (0.5 0.0 0.0), Y (0.0 0.5 0.0), and Z (0.0 0.0 0.5).

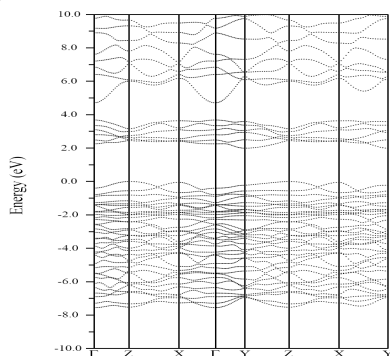


Fig. 5. Electronic bands along selected symmetry paths within the first Brillouin zone of CuWO_4 .

From Fig. 5 it is obvious that CuWO_4 is an indirect-gap material. This result confirms the similar suggestion by Ruiz-Fuertes et al. [43] based on measurements of optical-absorption spectra of CuWO_4 up to 18 GPa. From the band dispersions plotted in Fig. 5, we can make the following statement about the band extrema in CuWO_4 : the valence band has its maximum at the Γ point at the center of the Brillouin zone, while the minimum of the conduction band is located at the Y point (0.0 0.5 0.0). According to the present FP-LAPW calculations, the value of the indirect gap in CuWO_4 equals to 1.9988 eV. This value is slightly smaller as compared with the experimental value of the energy gap, E_g , of CuWO_4 ($E_g = 2.3$ eV) reported by Ruiz-Fuertes et al. [43] and that ($E_g = 2.06$ eV) derived experimentally for this tungstate by Benko et al. [44].

However, it is necessary to mention that first-principles calculations made within the GGA approximation [37] underestimate somewhat the energy gap of semiconductors and insulators. As a result, we can consider that the value $E_g = 1.9988$ eV obtained theoretically in the present FP-LAPW calculations for CuWO_4 is in good agreement with experimentally measured for this material values $E_g = 2.3$ eV [43] and $E_g = 2.06$ eV [44].

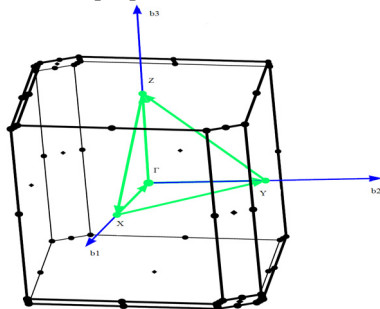


Fig. 6. Diagram of the Brillouin zone for a triclinic structure, which is characteristic of CuWO_4 , based on Ref. [42].

Some differences in the electronic structure of $M\text{WO}_4$ ($M = \text{Ca}, \text{Cd}, \text{Pb}$) compounds are obvious in the LAPW

calculations [40] and [41]: the minimum band gap of CaWO_4 is located at the Γ point at the center of the Brillouin zone, while the minimum band gaps do not occur at Γ for cadmium and lead tungstates. As it has been established the above mentioned authors, CdWO_4 reveals the minimum band gap at the Y point, which is located at the center of the Brillouin-zone boundary plane perpendicular to the b crystal axis, while PbWO_4 possesses band extrema at wave vectors away from the zone center (in the Σ and Δ directions) with possibly indirect band gaps.

Fig. 5 shows that the valence-band width of CuWO_4 equals about 7.7 eV. This result seems to be in agreement with those obtained in LAPW calculations of electronic properties of tungstates $M\text{WO}_4$ ($M = \text{Ca}, \text{Cd}, \text{Pb}$) [40] and [41]. Particularly, the valence-band width was evaluated to be about 7 eV for CdWO_4 with the wolframite-type structure [41]. This value is very close to that obtained in the present FP-LAPW calculations of CuWO_4 . For scheelite-type CaWO_4 and PbWO_4 compounds the LAPW calculations by Zhang et al. [40] have revealed somewhat smaller magnitudes of the valence-band widths, mainly 5 and 5.5 eV for calcium and lead tungstate, respectively.

The XPS W 4f core-level spectra of the $h\text{-WO}_3$ and CuWO_4 nanocrystals are presented in Fig. 7. It is apparent that the XPS W 4f core-level spectra in the both nanocrystalline materials under consideration are simple spin-doublets with the XPS W 4f_{7/2} binding energies corresponding to those of tungsten in the formal valence +6. It should be noted that values of the XPS O 1s core-level binding energies in the nanocrystals studied were found to be close to those in other representative tungsten-bearing wolframite-type [39] as well as $\text{KY}(\text{WO}_4)_2$ -type [45] tungstates.

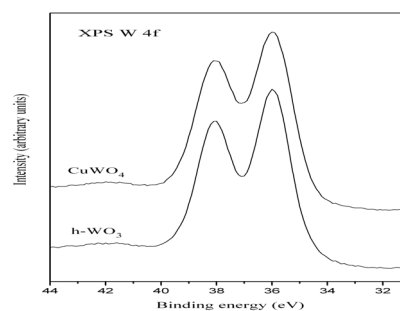


Fig. 7. XPS W 4f core-level spectra of $h\text{-WO}_3$ and CuWO_4 nanocrystals.

V. CONCLUSIONS

In summary, the electronic structure of $h\text{-WO}_3$ and CuWO_4 nanocrystals, prospective materials for renewable energy production and functional devices, was studied using X-ray photoelectron spectroscopy (XPS) and X-ray emission spectroscopy (XES). The XPS valence-band and core-level spectra as well as the XES W $L\beta_5$ and O $K\alpha$ bands representing the energy distribution of the W 5d- and O 2p-like states, respectively, were measured. Comparison on a common energy scale of the X-ray emission W $L\beta_5$ and O $K\alpha$ bands and the XPS valence-band spectra indicates that, the W 5d- and O 2p-like states contribute throughout the whole valence-band region of $h\text{-WO}_3$ and CuWO_4 nanocrystals, however maximum contributions of the O 2p-like states

occur in the upper, whilst the W 5d-like states in the lower portions of the valence band, respectively. Tungsten atoms in the both nanocrystalline materials are in the formal valence +6.

According to the present FP-LAPW calculations, CuWO_4 is an indirect-gap material: the valence band has its maximum at the Γ point at the center of the Brillouin zone, while the minimum of the conduction band is located at the Y point (0.0 0.5 0.0). The FP-LAPW calculations reveal the indirect gap of 1.9988 eV in CuWO_4 . This value is in reasonable agreement with the experimental energy gap values of CuWO_4 reported by Ruiz-Fuertes et al. [43] ($E_g = 2.3$ eV) and by Benko et al. [44] ($E_g = 2.06$ eV).

REFERENCES

- [1] M.A. Gondal, A. Hameed, and Z.H. Yamani, "Laser induced photocatalytic splitting of water over WO_3 catalyst," *Energy Sources*, vol. 27, pp. 1151-1165, 2005.
- [2] Lisha Zhang, Wenzhong Wang, Zhigang Chen, Lin Zhou, Haolan Xu, and Wei Zhu, "Fabrication of flower-like Bi_2WO_6 superstructures as high performance visible-light driven photocatalysts," *J. Mater. Chem.*, vol. 17, pp. 2526-2532, 2007.
- [3] F.E. Osterloh, "Inorganic materials as catalysts for photochemical splitting of water," *Chem. Mater.*, vol. 20, pp. 35-54, 2008.
- [4] A. Kudo and Y. Miseki, "Heterogeneous photocatalyst materials for water splitting," *Chem. Soc. Rev.*, vol. 38, pp. 253-278, 2009.
- [5] F. Zhang, M.Y. Sfeir, J.A. Misewich, and S.S. Wong, "Room-temperature preparation, characterization, and photoluminescence measurements of solid solutions of various compositionally-defined single-crystalline alkaline-earth-metal tungstate nanorods," *Chem. Mater.*, vol. 20, pp. 5500-5512, 2008.
- [6] Di Chen and Jinhua Ye, "Hierarchical WO_3 hollow shells: dendrite, sphere, dumbbell, and their photocatalytic properties," *Adv. Funct. Mater.*, vol. 18, pp. 1922-1928, 2008.
- [7] S. Rajagopal, D. Nataraj, D. Mangalaraj, Yahia Djaoued, Jacques Robichaud, and O.Yu. Khyzhun, "Controlled growth of WO_3 nanostructures with three different morphologies and their structural, optical, and photodecomposition studies," *Nanoscale Res. Lett.*, vol. 4, pp. 1335-1342, 2009.
- [8] A.M.-de la Cruz, D.S. Martínez, and E.L. Cuéllar, "Synthesis and characterization of WO_3 nanoparticles prepared by the precipitation method: Evaluation of photocatalytic activity under vis-irradiation," *Solid State Sci.*, vol. 12, pp. 88-94, 2010.
- [9] V.V. Atuchin, E.N. Galashov, A.S. Kozhukhov, L.D. Pokrovsky, and V.N. Shlegel, "Epitaxial growth of ZnO nanocrystals at $\text{ZnWO}_4(010)$ cleaved surface," *J. Cryst. Growth*, vol. 318, pp. 1147-1150, 2011.
- [10] E. Rossinyol, A. Prim, E. Pellicer, J. Arbiol, F. Hernández-Ramírez, F. Peiró, A. Cornet, J.R. Morante, L.A. Solovyov, Bozhi Tian, Tu Bo, and Dongyuan Zhao, "Synthesis and characterization of chromium-doped mesoporous tungsten oxide for gas-sensing applications," *Adv. Funct. Mater.*, vol. 17, pp. 1801-1806, 2007.
- [11] K.J. Lethy, D. Beena, R. Vinod Kumar, V.P. Mahadevan Pillai, V. Ganesan, V. Sathe, and D.M. Phase, "Nanostructured tungsten oxide thin films by reactive pulsed laser deposition technique," *Appl. Phys. A*, vol. 91, pp. 637-649, 2008.
- [12] Shibin Sun, Yimin Zhao, Yongde Xia, Zengda Zou, Guanghui Min, and Yanqiu Zhu, "Bundled tungsten oxide nanowires under thermal processing," *Nanotechnology*, vol. 19, pp. 305709, 2008.
- [13] V.V. Atuchin, E.N. Galashov, O.Yu. Khyzhun, A.S. Kozhukhov, L.D. Pokrovsky, and V.N. Shlegel, "Structural and electronic properties of $\text{ZnWO}_4(010)$ cleaved surface," *Cryst. Growth Des.*, vol. 11, pp. 2479-2484, 2011.
- [14] V.V. Atuchin and B.I. Kidyarov, "Classification and search for novel binary acentric molybdate and wolframite crystals," *J. Korean Cryst. Growth Cryst. Technol.*, vol. 12, pp. 323-328, 2002.
- [15] V.V. Atuchin, B.I. Kidyarov, and N.V. Pervukhina, "Phenomenological modeling and design of new acentric crystal for optoelectronics," *Comput. Mater. Sci.*, vol. 30, pp. 411-418, 2004.
- [16] B.I. Kidyarov and V.V. Atuchin, "Universal crystal classification system "Point symmetry – physical property," *Ferroelectrics*, vol. 360, pp. 96-99, 2007.
- [17] B.I. Kidyarov and V.V. Atuchin, "Interrelationship of micro- and macro-structure and physical properties of binary acentric oxide ferroelastic and paraelastic crystals," *Ferroelectrics*, vol. 360, pp. 104-110, 2007.
- [18] S. Rivier, X. Mateos, V. Petrov, U. Griebner, Y.E. Romanyuk, C.N. Borca, F. Gardillou, and M. Pollnau, "Tm:KY(WO_4)₂ waveguide laser," *Opt. Express*, vol. 15, pp. 5885-5892, 2007.
- [19] M. Pollnau, Y.E. Romanyuk, F. Gardillou, C.N. Borca, U. Griebner, S. Rivier and V. Petrov, "Double tungstate lasers: From bulk toward on-chip integrated waveguide devices," *IEEE J. Select. Topics Quant. Elect.*, vol. 13, pp. 661-671, 2007.
- [20] S. Garcia-Revilla, R. Valiente, Y.E. Romanyuk, and M. Pollnau, "Temporal dynamics of upconversion luminescence in Er^{3+} , Yb^{3+} co-doped crystalline $\text{KY}(\text{WO}_4)_2$ thin films," *J. Luminescence*, vol. 128, pp. 934-936, 2009.
- [21] O.Yu. Khyzhun, Yu.M. Solonin, and V.D. Dobrovolsky, "Electronic structure of hexagonal tungsten trioxide: XPS, XES, and XAS studies," *J. Alloys Compd.*, vol. 320, pp. 1-6, 2001.
- [22] V.V. Atuchin, V.G. Kesler, N.Yu. Maklakova, and L.D. Pokrovsky, "Core level spectroscopy and RHEED analysis of $\text{KGd}(\text{WO}_4)_2$ surface," *Solid State Commun.*, vol. 133, pp. 347-351, 2005.
- [23] V.L. Bekenev, O.Yu. Khyzhun, and V.V. Atuchin, "Electronic structure of monoclinic α -KY(WO_4)₂ tungstate as determined from first-principles FP-LAPW calculations and X-ray spectroscopy studies," *J. Alloys Compd.*, vol. 485, pp. 51-58, 2009.
- [24] V.V. Atuchin, T.A. Gavrilova, V.G. Kostrovsky, L.D. Pokrovsky, and I.B. Troitskaia, "Morphology and structure of hexagonal MoO_3 nanorods," *Inorg. Mater.*, vol. 44, pp.622-627, 2008.
- [25] C.V. Ramana, V.V. Atuchin, I.B. Troitskaia, S.A. Gromilov, V.G. Kostrovsky, and G.B. Sauep, "Low-temperature synthesis of morphology controlled metastable hexagonal molybdenum trioxide (MoO_3)," *Solid State Commun.*, vol.149, pp. 6-9, 2009.
- [26] V.V. Atuchin, T.A. Gavrilova, S.A. Gromilov, V.G. Kostrovsky, L.D. Pokrovsky, I.B. Troitskaia, R.S. Vemuri, G. Carbajal-Franco, and C.V. Ramana, "Low-temperature chemical synthesis and microstructure analysis of GeO_2 crystals with α -quartz structure," *Cryst. Growth Des.*, vol. 9, pp. 1829-1832, 2009.
- [27] C.V. Ramana, I.B. Troitskaia, V.V. Atuchin, M. Ramos, and D. Ferrer, "Electron microscopy characterization of hexagonal molybdenum trioxide (MoO_3) nanorods," *J. Vac. Sci. Technol. A*, vol. 28, pp. 726-729, 2010.
- [28] C.V. Ramana, G. Carbajal-Franco, R.S. Vemuri, I.B. Troitskaia, S.A. Gromilov, and V.V. Atuchin, "Optical properties and thermal stability of germanium oxide (GeO_2) nanocrystals with α -quartz structure," *Mater. Sci. Eng. B*, vol. 174, pp. 279-284, 2010.
- [29] I.B. Troitskaia and T.A. Gavrilova, "Nanoplates of h - WO_3 : synthesis, micromorphology, characterization," *Lett. Mater.* vol. 1, pp. 65-69, 2011.
- [30] O.Yu. Khyzhun and Yu.M. Solonin, "Electronic structure of hexagonal hydrogen tungsten bronze H_3WO_3 nanoparticles, a prospective sensor material," *Int. Sci. J. Alternat. Energy Ecology*, vol. 6, pp. 52-55, 2002.
- [31] O.Yu. Khyzhun, T. Strunskus, S. Cramm, and Yu.M. Solonin, "Electronic structure of CuWO_4 : XPS, XES and NEXAFS studies," *J. Alloys Compd.*, vol. 389, pp. 14-20, 2005.
- [32] V.V. Atuchin, V.G. Kesler, N.Yu. Maklakova, L.D. Pokrovsky, and D.V. Sheglov, "Core level spectroscopy and RHEED analysis of $\text{KGd}_{0.95}\text{Nd}_{0.05}(\text{WO}_4)_2$ surface," *Eur. Phys. J. B*, vol. 51, pp. 293-300, 2006.
- [33] O.Yu. Khyzhun, V.L. Bekenev, and Yu.M. Solonin, "First-principles calculations and X-ray spectroscopy studies of the electronic structure of CuWO_4 ," *J. Alloys Compd.*, vol. 480, pp. 184-189, 2009.
- [34] V.L. Bekenev, O.Yu. Khyzhun, A.K. Sinelnichenko, V.V. Atuchin, O.V. Parasyuk, O.M. Yurchenko, Yu. Bezsmolnyj, A.V. Kityk, J. Szkutnik, S. Calus, "Crystal growth and the electronic structure of Tl_3PbCl_5 ," *J. Phys. Chem. Solids*, vol. 72, pp. 705-713, 2011.
- [35] P. Blaha, K. Schwarz, and J. Luitz, "WIEN97, A full potential linearized augmented plane wave package for calculating crystal properties," Technical University, Vienna, 1999.
- [36] L. Kihlberg and E. Gebert, " CuWO_4 , a distorted Wolframite-type structure," *Acta Cryst. B*, vol. 26, pp. 1020-1025, 1970.
- [37] J.P. Perdew, S. Burke, and M. Ernzerhof, "Generalized Gradient Approximation Made Simple," *Phys. Rev. Lett.*, vol. 77, pp. 3865-3868, 1996.
- [38] P.E. Blöchl, O. Jepsen, and O.K. Andersen, "Improved tetrahedron method for Brillouin-zone integrations," *Phys. Rev. B*, vol. 49, pp. 16223-16233, 1994.
- [39] S. Rajagopal, D. Nataraj, O.Yu. Khyzhun, Y. Djaoued, J. Robichaud, D. Mangalaraj, "Hydrothermal synthesis and electronic properties of FeWO_4 and CoWO_4 ," *J. Alloys Compd.*, vol. 493, pp. 340-345, 2010.

- [40] Y. Zhang, N.A.W. Holzwarth, and R.T. Williams, "Electronic band structures of scheelite materials – CaMoO_4 , CaWO_4 , PbMoO_4 , and PbWO_4 ," *Phys. Rev. B*, vol. 57, pp. 12738-12750, 1998.
- [41] Y. Abraham, N.A.W. Holzwarth, and R.T. Williams, "Electronic Structure and Optical Properties of CdMoO_4 and CdWO_4 ," *Phys. Rev. B*, vol. 62, pp. 1733-1741, 2000.
- [42] A. Kokalj, "Computer graphics and graphical user interfaces as tools in simulations of matter at the atomic scale," *Comp. Mater. Sci.*, vol. 28, pp. 155-168, 2003.
- [43] J. Ruiz-Fuertes, D. Errandonea, A. Segura, F.J. Manjón, Zh. Zhu, C.Y. Tu, "Growth, characterization, and high-pressure optical structure of CuWO_4 ," *High Pres. Res.*, vol. 28, pp. 565-570, 2008.
- [44] F.A. Benko, C.L. MacLaurin, and F.P. Koffyberg, " CuWO_4 and Cu_2WO_6 as anodes for the photoelectrolysis of water," *Matter. Res. Bulletin*, vol. 17, pp. 133-136, 1982.
- [45] V.V. Atuchin, L.D. Pokrovsky, O.Yu. Khyzhun, A.K. Sinelnichenko, and C.V. Ramana, "Surface crystallography and electronic structure of potassium yttrium tungstate," *J. Appl. Phys.*, vol. 104, pp. 033518, 2008.



Victor V. Atuchin was born in Prokopiyevs'k / Russia on August, 1957. He received the diploma degree in radiophysics from the Tomsk State University, Tomsk/Russia in 1979 and the Ph.D. degree in solid state physics from the Institute of Semiconductor Physics of SB of RAS, Novosibirsk/Russia, in 1993. In 1980, he joined the Institute of Semiconductor Physics as an Engineer of Electronics, and as Head of Laboratory of Optical Materials and Structures in July 2002. Since 1980, his principal research interests have been in the fields of solid state physics, and materials science. His interests include fabrication and characterization of thin films, surface science and chemistry of oxide crystals. He is the author or coauthor of 189 publications in refereed journals. Prof. Atuchin is a member of IUCr.



Irina B. Troitskaia was born in Novosibirsk / Russia on April, 1968. She received the diploma in chemistry and technology of basic organic and petrochemical synthesis degree from the Tomsk Polytechnic University. In 2005, he joined the Institute of Semiconductor Physics as an Engineer. Her principal research interests are the synthesis of transition metal oxide crystals, investigation and systematization of their physico-chemical characteristics. She is the author or coauthor of 8 publications in refereed journals and 2 patents.



Oleg Yu. Khyzhun, was born in Volyn Region / Ukraine on August, 1962. He received the diploma degree in physics and mathematics from National Volyn University, Lutsk/Ukraine in 1982 and the Ph.D. and D.Sc. degrees in solid state physics from Frantsevich Institute for Problems of Materials Science, NAS of Ukraine, Kiev/Ukraine, in 1992 and 2005, respectively. In 1986, he joined Frantsevich Institute for Problems of Materials Science as a post-graduate student, and as Head of Surface Science Laboratory in 2010. Since 1986, his principal research interests have been in the fields of solid state physics, and materials science. His interests include mainly a study of the electronic structure of solids. He is the author or coauthor of 96 publications in refereed journals. Prof. Khyzhun is a member of Ukrainian Physical Society and Ukrainian Materials Society.



Valeriy I. Bekenev, was born in Rostov-on-Don/ Russia on August, 1946. He received the diploma degree in solid state physics from the Rostov-on-Don State University in 1969. In 1970, he joined Frantsevich Institute for Problems of Materials Science, NAS of Ukraine, Kiev/Ukraine as a post-graduate student, and as a researcher of the Department of Applied Physics and Computer Modeling in Material Science in 2000. Since 1970, his principal research interests have been in the fields of solid state physics. His interests include first-principles electronic structure calculations of solids and surfaces, computational studies of nanostructures and clusters, molecular dynamic simulations of different kind of materials. He is the author or coauthor of 45 publications in refereed journals. Mr. Bekenev is a member of Ukrainian Materials Society.



Yuriy M. Solonin, was born in Novokuznetsk/ Russia on April, 1942. He received the diploma degree in metal physics from the National Technical University "Kiev Polytechnic Institute", Kiev/Ukraine in 1964 and the Ph.D. and D.Sc. degrees in solid state physics from Frantsevich Institute for Problems of Materials Science, NAS of Ukraine, Kiev/Ukraine, in 1974 and 1990, respectively. In 1964, he joined Frantsevich Institute for Problems of Materials Science as an engineer, and as Head of Department of Structural Chemistry of Solids in 1996. Since 2003, he is a deputy director of Frantsevich Institute for Problems of Materials Science. His principal research interests have been in the fields of materials science. His interests include fabrication and characterization of thin films and bulk materials of transition metals oxides, mainly Magneli phases, as well as studies of the electronic structure and hydrogen-sorption properties of hydrides and hydride-forming alloys. He is the author or coauthor of 204 publications in refereed journals. Prof. Solonin is a member of Ukrainian Materials Society.