Optical absorption of divalent metal tungstates: Correlation between the band-gap energy and the cation ionic radius

R. Lacomba-Perales, J. Ruiz-Fuertes, D. Errandonea(a), D. Martínez-García and A. Segura

MALTA Consolider Team, Departamento de Física Aplicada-ICMUV, Universitat de València, Edificio de Investigación - C/Dr. Moliner 50, 46100 Burjassot (Valencia), Spain, EU

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Abstract – We have carried out optical-absorption and reflectance measurements at room temperature in single crystals of AWO_4 tungstates (A = Ba, Ca, Cd, Cu, Pb, Sr, and Zn). From the experimental results their band-gap energy has been determined to be 5.26 eV (BaWO_4), 5.08 eV (SrWO_4), 4.94 eV (CaWO_4), 4.15 eV (CdWO_4), 3.0–4.4 eV (ZnWO_4), 3.8–4.2 eV (PbWO_4), and 2.3 eV (CuWO_4). The results are discussed in terms of the electronic structure of the studied tungstates. It has been found that those compounds where only the s electron states of the A^{2+} cation hybridize with the O 2p and W 5d states (e.g., BaWO_4) have larger band-gap energies than those where also p, d, and f states of the A^{2+} cation contribute to the top of the valence band and the bottom of the conduction band (e.g., PbWO_4). The results are of importance in view of the large discrepancies existing in previously published data.

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Introduction. – Metal tungstates (AWO_4) are semiconductors which usually crystallize in the tetragonal scheelite structure (I4_1/a) [1], for large A^{2+} cations (A = Ba, Ca, Eu, Pb, Sr), or in the monoclinic wolframite structure (P2_1/c), for small A^{2+} cations (A = Co, Cd, Fe, Mg, Ni, Zn) [2]. In scheelite W is coordinated by four O forming WO_4 tetrahedra, while in wolframite W is surrounded by six O forming WO_6 octahedra. Other tungstates crystallize in structures related to scheelite, like monoclinic HgWO_4 (C2/c) [3] and cubic SnWO_4 (P2_13) [4], or to wolframite, like triclinic (CuWO_4 (P1)) [5]. Nowadays, metal tungstates attract the attention of crystal-growth scientists, radiologists, and physicists due to their applications in the field of photonics and photoelectronics [6]. Their use in the detectors of the Large Hadron Collider at CERN [7], as laser-host materials [8], and in other optoelectronic devices like eye-safe Raman lasers [9] also attracted a lot of attention on them. For all these applications an accurate knowledge of the band-gap energy (E_g) of tungstates is needed. However, despite the efforts made in the past, up to now no agreement concerning E_g in metal tungstates was reached. The analysis of the literature data shows that the measured values of E_g are widely dispersed (see table 1) [10–21]. In the particular cases of CaWO_4 [9] and ZnWO_4 [10], E_g ranges from 4.4 to 6.8 eV and from 3.8 to 5.7 eV, respectively. It is, therefore, evident that E_g in metal tungstates cannot be regarded as being accurately determined. In the present work we have measured E_g for BaWO_4, SrWO_4, CaWO_4, CdWO_4, ZnWO_4, PbWO_4, and CuWO_4 by means of reflectance and optical-absorption measurements. This approach has been previously probed to be very useful for obtaining E_g accurately in many semiconductors [22].

Experimental details. – The samples used in the absorption experiments were thin platelets cleaved along natural cleavage directions of single crystals grown with the Czochralski method starting from commercial raw powders having 5N purity. More details on the crystal growth can be found elsewhere [7,9,23–25]. The thickness of the studied specimens ranged from 10 to 30 μm and their size was about 1000 μm × 1000 μm. In the reflectance measurements we used polished crystal plates 3–10 mm thick. The as-grown crystals were colorless with the exception of the CuWO_4 crystal which had a dark-brown color. These crystals were characterized by X-ray diffraction. The obtained diffraction patterns corresponded to the structures reported in the literature for the seven tungstates. No indication of any extra phase was found in any of them. For the optical-absorption measurements in
Table 1: $E_g$ and effective ionic radius [33] for different tungstates. The index "a" stands for measured values, and "b" for estimated values. The literature data were taken from refs. [10–21].

| Compound  | $E_g$ (eV) | Ionic radius of cation A (Å) |
|-----------|------------|-----------------------------|
| BaWO$_4$  | 4.8–5.2    | 1.42                        |
| SrWO$_4$  | 4.56       | 1.26                        |
| CaWO$_4$  | 4.4–6.8    | 1.12                        |
| HgWO$_4$  | 4.55$^b$   | 1.02                        |
| CdWO$_4$  | 4–5        | 0.95                        |
| ZnWO$_4$  | 3.8–5.7    | 0.74                        |
| MgWO$_4$  | 3.9        | 0.72                        |
| PbWO$_4$  | 3.7–4.7    | 1.29                        |
| EuWO$_4$  | 3.7$^b$    | 1.25                        |
| CuWO$_4$  | 2.1–3.6    | 0.73                        |
| SnWO$_4$  | 2.6        | 0.69                        |
| NiWO$_4$  | 2.28       | 0.69                        |
| CoWO$_4$  | 2.43$^b$   | 0.65                        |
| FeWO$_4$  | 2.35$^b$   | 0.61                        |

In order to determine $E_g$, we have analyzed the measured absorption spectra of all the studied tungstates, but CuWO$_4$, assuming that the band-gap is of direct type and that the absorption edge obeys Urbach’s rule $\alpha = A_0 e^{\left(-E/U - h\nu\right)/E_U}$ [29]. In this equation $E_U$ is Urbach’s energy, which is related to the steepness of the absorption tail, and $A_0 = k\sqrt{E_U}$ for a direct band-gap [18], being $k$ a characteristic parameter of each material. Figure 2 illustrates the quality of the fits we obtained for our data using this model. As can be seen, the agreement of the fits with the experiments is quite good. For CuWO$_4$ we considered an indirect band-gap and $E_g$ was determined by plotting the square root of $\alpha$ and extrapolating a linear fit to zero (see fig. 2). The results obtained by applying these analyses are summarized in table 1. In particular, we found that $E_g$ decreases following the sequence BaWO$_4 >$ SrWO$_4 >$ CaWO$_4 >$ CdWO$_4 >$ ZnWO$_4 >$ PbWO$_4 >$ CuWO$_4$. For BaWO$_4$, the determined $E_g$ agrees well with the values reported in the literature [19]. In the case of CaWO$_4$, the measured $E_g$ is 4.94 eV. This value is in agreement with that obtained by two-photon excitation techniques [11] suggesting that
the band-gap energy of calcium tungstate is significantly lower than the previously accepted value (6.8 eV). For CaWO$_4$, Arora et al. obtained $E_g = 4.6$ eV from optical measurements similar to ours [10]. For SrWO$_4$ they obtained $E_g = 4.56$ eV, while we obtained $E_g = 5.08$ eV. We think that their underestimation of $E_g$ and their conclusion that CaWO$_4$ and SrWO$_4$ are indirect band-gap semiconductors were possibly caused by the fact that they used thick samples in their experiments. As a consequence of this, the defect-related low-energy tail could have been misinterpreted as a part of the fundamental absorption, leading to a different characterization of the band-gap and to an underestimation of its energy. In other compounds like ZnWO$_4$, CdWO$_4$, and PbWO$_4$ our results are also, like in CaWO$_4$, close to the lowest $E_g$ values found in the literature (see table 1). In particular, for PbWO$_4$ our results agree with those reported by Itoh et al. [12,14]. Regarding CuWO$_4$, we found $E_g = 2.3$ eV. This value is 1.3 eV smaller than the one previously reported by Arora et al. [17]. However, it is only 0.2 eV larger than the value obtained recently from thin films of CuWO$_4$ by Pandey et al. [16]. As the typical reduction of $E_g$ in thin films is about 0.2 eV [26] it seems that $E_g$ was previously overestimated in CuWO$_4$.

In the inset of fig. 1 we show our reflectance measurements. For CuWO$_4$, we did not find any structure in the reflectance spectrum at the band-gap photon energy, which is consistent with the indirect character of its band-gap. For PbWO$_4$ and ZnWO$_4$, a clear maximum can be seen in the reflectance spectra. According to the position of these maxima, we determined $E_g = 4.2$ and 4.4 eV, respectively. These values are slightly higher than the values obtained from the absorption measurements but still on the lower limit of the large dispersion of values reported for $E_g$ in the literature. In the cases of the alkaline-earth tungstates, the band-gap cannot be determined from the reflectance measurements since it is located very close to the high-photon energy limit of our spectrometer. As a consequence of this, there is no maximum present in the reflectance spectra (see inset of fig. 1).

Density-functional theory [20], discrete variational [21], and ab initio [30] electronic-structure calculations indicate that in scheelite- and wolframite-structured tungstates the upper part of the valence band consists mainly of the O$^{2-}2p$ states, and the conduction band is dominated by the W$^{6+}5d$ states, in a similar way as it occurs in WO$_3$ [31]. The same conclusion was drawn for SnWO$_4$ [18]. The splitting caused by the crystal field in the O$^{2-}2p$ states and the W$^{6+}5d$ states produces the increase of $E_g$ with respect to WO$_3$ [20]. In addition, when the bivalent $A^{2+}$ cation of the tungstate belongs to group numbers 2 or 12 of the Periodic Table (i.e. the valence shell of A contains only s electrons), the s orbitals make some contribution to the valence and conduction bands. On the other hand, if A is a transition metal, an element of group number 14 of the Periodic Table, or a lanthanide, the O$^{2-}2p$ states and the W$^{6+}5d$ also hybridizes with the p, d, or f electrons of the A$^{2+}$ cation. Therefore the metal states contribution to the valence and conduction bands is more important. These conclusions have been confirmed by X-ray photoelectron spectroscopy measurements performed in BaWO$_4$, CaWO$_4$, CdWO$_4$, ZnWO$_4$, PbWO$_4$, and CuWO$_4$ [21,32]. According to our results, the first group of bivalent metals leads to compounds with a larger $E_g$ than the second group (see table 1). We also observed that for both groups of tungstates a correlation can be established between the effective ionic (Shannon) radius [33] of the A$^{2+}$ metal and $E_g$. In fig. 3 we plotted $E_g$ vs. the Shannon radii of A. There it can be seen that for those elements whose valence shell contains only s electrons (Mg, Ca, Sr, Ba, Zn, Cd) there is a direct correlation between $E_g$ and the ionic radius; i.e., the bigger the A$^{2+}$ cation the larger the band-gap of the AWO$_4$ compound. A similar trend is followed by those compounds with bivalent cations with a different electronic configuration (Pb, Sn, Cu, Ni), but in that case $E_g$ is systematically 1.4 eV smaller than in the former one. The smaller band-gap of the second group of compounds could be caused by the larger contribution of the metal states to the valence and conduction bands. Was this hypothesis correct, the pressure effects on the band-structure of the second group of compounds should be more important than in the first group. On the other hand, the correlation we established between $E_g$ and the ionic radius is coherent with the fact that electron states hybridization is expected to be affected by the size of the A$^{2+}$ cation [34].

Fig. 2: Room temperature absorption spectra of SrWO$_4$ and ZnWO$_4$ showing the fits used to determine $E_g$. Dots: experiments. Lines: fits. The inset shows the $\alpha^{1/2}$ vs. photon energy plot for CuWO$_4$ to illustrate the indirect character of its band-gap.
Moreover, the correlation we found can be used to make a back-of-the-envelope estimation of the \( E_g \) in other tungstates. We estimated \( E_g = 4.55 \text{ eV} \) (HgWO\(_4\)), 3.92 \text{ eV} (MgWO\(_4\)), 3.79 \text{ eV} (EuWO\(_4\)), 2.52 \text{ eV} (SnWO\(_4\)), 2.52 \text{ eV} (NiWO\(_4\)), 2.43 \text{ eV} (CoWO\(_4\)), and 2.35 \text{ eV} (FeWO\(_4\)). The predictions made for MgWO\(_4\), SnWO\(_4\), and NiWO\(_4\) agree fairly well with previous experiments \cite{15,16,18} supporting the correctness of the predictions made for the other four compounds, which however should be tested by future experiments and \textit{ab initio} calculations. Finally, the lines drawn in fig. 3 can be also used to predict \( E_g \) in solid solutions of different tungstates (e.g., Zn\(_2\)Ni\(_{1-x}\)WO\(_4\)) which as a first approximation can be assumed to vary linearly with the composition of the solid solutions \cite{35}.

**Conclusions.** — In summary, the absorption and reflectance spectra of BaWO\(_4\), SrWO\(_4\), CaWO\(_4\), CdWO\(_4\), ZnWO\(_4\), PbWO\(_4\), and CuWO\(_4\) have been accurately measured at room temperature. Our measurements suggest that all the studied compounds are direct band-gap semiconductors with the exception of CuWO\(_4\) which is an indirect band-gap material. In addition, they allowed for a precise determination of \( E_g \) in the seven studied tungstates and to solve pre-existent discrepancies. We also found that in those compounds where the hybridization of the A metal states with W and O states is more important the band-gap is smaller than in those compounds where this hybridization is smaller.

Based upon previous calculations, the reported results are explained in terms of the electronic structure of tungstates. Finally, a correlation between \( E_g \) and the Shannon radii of the bivalent cation A was empirically found. This correlation is shown to be consistent with the present understanding of the electronic structure of tungstates and can be used to predict \( E_g \) for unstudied tungstates like HgWO\(_4\).

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**REFERENCES**

\[1\] Errandonea D., Phys. Status Solidi (b), 242 (2005) R125.
\[2\] Sleight A. W., Acta Crystallogr. B, 28 (1972) 2899.
\[3\] Jeitschko W. and Sleight A. W., Acta Crystallogr. B, 29 (1973) 869.
\[4\] Jeitschko W. and Sleight A. W., Acta Crystallogr. B, 28 (1972) 3174.
\[5\] Schofield P. F. and Redfern S. A. T., J. Phys.: Condens. Matter, 4 (1992) 375.
\[6\] Errandonea D., EPL, 77 (2007) 56001; Errandonea D. and Manión F. J., Prog. Mater. Sci., 53 (2008) 711.
\[7\] Lecocq P., Dafinei L., Affragn J. V., Schergans M., Kozhik M. V., Missetich O. V., Pavlenko V. B., Fedorov A. A., Annenkov A. N., Kostylev V. L. and Ligun V. D., Nucl. Instrum. Methods Phys. Res. A, 365 (1995) 291.
\[8\] Faure N., Borel C., Coumaud G., Basset G., Templier R. and WYON C., Appl. Phys. B, 63 (1996) 593.
\[9\] Nikl M., Bohacek P., Mihokova N., Kobayashi M., Ishii M., Usuki Y., et al., J. Lumin., 87-89 (2000) 1136.
\[10\] Arora S. K. and Chudasama B., Cryst. Res. Technol., 41 (2006) 1089.
\[11\] Mikhailik V. B., Kraus H., Wail D., Itoh M., Liske M. and Bailiff I. K., Phys. Rev. B, 69 (2004) 205110.
\[12\] Itoh M., Katagiri T., Tani Y. and Fujita M., Radiat. Meas., 42 (2007) 545; Nagirny V., Kirm M., Kotlov A., Lushchik A. and Jonsson L., J. Lumin., 102 (2003) 597 and references therein.
\[13\] Garcés N. Y., Chirla M. M., Murphy H. J., Foise J. W., Thomas E. A., Wicks C., Grecenwicz K., Halliburton L. E. and Giles N. C., J. Phys. Chem. Solids, 64 (2003) 1195; Xiao H., Chen H., Xu F., Jiang C. and Yang P., J. Cryst. Growth, 310 (2008) 521.
\[14\] Errandonea D., Martinez-Garcia D., Lacomba-Perales R., Ruiz-Fuertes J. and Segura A., Appl. Phys. Lett., 89 (2006) 091913; Itoh M., Yokota H., Horigoto M., Fujita M. and Usuki Y., Phys. Status Solidi (b), 231 (2002) 595.
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[15] Saito N., Sonoyama N. and Sakata T., Bull. Chem. Soc. Jpn., 69 (1996) 2191.
[16] Pandey P. K., Bhave N. S. and Kharat R. B., Electrochim. Acta, 51 (2006) 4659.
[17] Arora S. K., Matthew T. and Batra N. M., J. Phys. Chem. Solids, 50 (1989) 665; Pandey P. K., Bhave N. S. and Kharat R. B., Mater. Lett., 59 (2005) 3149.
[18] Stoltzfus M. W., Woodward P. M., Seshadri R., Klepeis J. H. and Bursten B., Inorg. Chem., 46 (2007) 3839.
[19] Ran D. G., Xia H. R., Sun S. Q., Zhao P., Liu F. Q., Ling Z. C., Ge W. W., Zhang H. J. and Wang J. Y., Cryst. Res. Technol., 41 (2006) 1189.
[20] Abraham Y., Holzwarth N. A. W. and Williams R. T., Phys. Rev. B, 62 (2000) 1733; Zhang Y., Holzwarth N. A. W. and Williams R. T., Phys. Rev. B, 57 (1998) 12738.
[21] Itoh M., Fujita N. and Inabe Y., J. Phys. Soc. Jpn., 75 (2006) 084705.
[22] Ruiz-Fuertes J., Errandonea D., Manjón F. J., Martínez-García D., Segura A., Ursaki V. V. and Tiginyanu I. M., J. Appl. Phys., 103 (2008) 063710.
[23] Brice J. C. and Wiffen P. A. C., Br. J. Appl. Phys., 18 (1967) 581.
[24] Yang F. G., Tu C. Y., Wang H. Y., Wei Y. P., You Z. Y., Jia G. H., Li J. F., Zhu Z. J., Lu X. A. and Wang Y., J. Alloys Compd., 455 (2008) 269.
[25] Errandonea D., Tu C. Y., Ha G. H., Martin I. R., Rodriguez-Mendoza U. R., Larioz F., Torres M. E. and Lavin V., J. Alloys Compd., 451 (2008) 212.
[26] Segura A., Sanz J. A., Errandonea D., Martínez-García D. and Fages V., Appl. Phys. Lett., 88 (2006) 011910.
[27] Niki M., Phys. Status Solidi (a), 178 (2000) 595; Lin Q., Feng X., Man Z., Shi Z. and Zhang Q., Phys. Status Solidi (a), 181 (2000) R1.
[28] Fujita M., Itoh M., Horimoto M. and Yokota H., Phys. Rev. B, 65 (2002) 195105.
[29] Urbach F., Phys. Rev., 92 (1953) 1324.
[30] Rodríguez-Hernandez P. and Muñoz A., private communication.
[31] Hjelm A., Granqvist C. G. and Wills J. M., Phys. Rev. B, 54 (1996) 2436.
[32] Khyzhun O. Y., Strunskus T., Cramm S. and Solonin Y. M., J. Alloys Compd., 389 (2005) 14.
[33] Shannon R. D., Acta Crystallogr. A, 32 (1976) 751.
[34] Errandonea D., Boehler R. and Ross M., Phys. Rev. B, 65 (2002) 012108; Skriver H. L., Phys. Rev. B, 31 (1985) 1909.
[35] de Oliveira A. L. M., Ferreira J. M., Silva M. R. S., Braga G. S., Soledade L. E. B., Maurera M. A., Paskocimas C. A., Lima S. J. G., Longo E., de Souza A. G. and García dos Santos I. M., Dyes Pigm., 77 (2008) 210.