High-pressure characterization of the optical and electronic properties of InVO_4 , InNbO_4 , and InTaO_4

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Abstract

We have studied the electronic properties at ambient pressure and under high pressure of InVO_4 , InNbO_4 , and InTaO_4 powders, three candidate materials for hydrogen production by means of photocatalytic water splitting using solar energy. A combination of optical absorption and resistivity measurements and band structure calculations have allowed us to determine that these materials are wide band-gap semiconductors with a band-gap energy of 3.62(5), 3.63(5), and 3.79(5) eV for InVO_4 , InNbO_4 , and InTaO_4 , respectively. The last two compounds are indirect band-gap materials, and InVO_4 is a direct band-gap material. The pressure dependence of the band-gap energy and the electrical resistivity have been determined too. In the three compounds, the band gap opens under compression until reaching a critical pressure, where a phase transition occurs. The structural transition triggers a band-gap collapse larger than 1.2 eV in the three materials, being the abrupt decrease in the band-gap energy related to an increase in the pentavalent cation coordination number. The phase transitions also cause changes in the electrical resistivity, which can be correlated with changes induced by pressure in the band structure. An explanation to the reported results is provided based upon *ab initio* calculations. The conclusions attained are of significance for technological applications of the studied oxides.

Keywords Wolframite · Band gap, optical properties · High pressure · Phase transition · Electronic properties

1 Introduction

Many ternary metal oxide compounds of the form AMO_4 have been extensively studied during the last decade due to their physical properties and technological applications including their low cost and environment friendliness [1–6]. Among this family of oxides, InMO_4 compounds ($\text{M} = \text{V}^{5+}$, Nb^{5+} , or Ta^{5+}) are of particular interest due to their excellent photocatalytic activity for water splitting under visible-light irradiation [7, 8]. Their photocatalytic properties have been empirically correlated to the crystal structure [7, 8], but their electronic structure has not yet

been understood completely. In particular, the band-gap energy (E_g), a magnitude fundamental for developing the proposed technological applications, has not been accurately reported for any of the compounds. A precise determination of E_g can be achieved by means of optical absorption measurements. In addition, high-pressure (HP) studies have proven to be a formidable tool to test the robustness of the understanding of the electronic structure achieved by means of ambient-conditions studies in semiconductors [9].

InNbO_4 and InTaO_4 are isostructural compounds which crystallize in the wolframite structure [10]. They belong to

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the monoclinic space group $P2_1/c$, having two formula units per unit cell ($Z=2$). In this structure, In and Nb(Ta) cations have an octahedral oxygen coordination. Under HP, both compounds undergo a phase transition to another monoclinic phase [11, 12]. The transformation to the HP phase involves a coordination increase in In and Nb(Ta). InVO_4 crystallizes in a different structure compared to InNbO_4 and InTaO_4 . This structure belongs to the orthorhombic space group Cmcm ($Z=4$) [13]. The structure has InO_6 octahedral units and VO_4 tetrahedral units as building blocks. Under compression, InVO_4 undergoes a phase transition to a wolframite-type structure [14].

Regarding the electronic properties of InMO_4 compounds, the common feature is that the states at the bottom of the conduction bands are composed mainly of V 3d, Nb 4d, or Ta 5d electronic levels. On the other hand, O 2p states dominate the upper part of the valence bands. However, in the literature, it can be seen that there are significant discrepancies in the reported E_g values, which range from 1.8 to 4.8 eV, as well as about their band-gap nature, i.e., indirect or direct transition [11, 15–26]. In fact, in some studies, the absorption of light by defects has been mistakenly assigned to the fundamental band gap [11].

Recently, optical absorption experiments together with band structure calculations clarified the discrepancies in the case of InTaO_4 [11]. This work showed that InTaO_4 is a wide indirect-gap semiconductor with $E_g = 3.79(5)$ eV, and the previous reports underestimated the band-gap value by 1.2 eV [15, 16]. In addition, investigations under HP have played an important role in the clarification of the nature of fundamental band gap. Such studies have also been shown to be an excellent tool for improving the knowledge of the influence of structural modifications on physical properties of InVO_4 [14], InNbO_4 [12], and InTaO_4 [11]. One of the interesting phenomena observed in these compounds under compression is the color changes associated with the HP phase transition. In InTaO_4 , the color change has been related to an increase in the coordination number of Ta. Similar changes in the coordination number also occur in InNbO_4 [12] and InVO_4 [14], suggesting that HP might also trigger interesting changes in their electronic properties, reducing the band gap to values close to 2 eV, which might improve their photocatalytic activity [27].

To further understand the electronic behavior of InVO_4 , InNbO_4 , and InTaO_4 at ambient pressure and under HP, we have performed a combined experimental and theoretical study. Optical absorption measurements have been carried out up to 16 GPa (20 GPa) for InVO_4 (InNbO_4). Resistivity measurements have been performed in the three compounds up to 10 GPa, and first-principles band structure calculations have been carried out for InNbO_4 . The

results of these studies have been combined with optical measurements previously reported by us for InTaO_4 [11] and band structure calculations already published by us for InTaO_4 and InVO_4 [11, 14]. Based upon all the studies mentioned above, we report an accurate determination of E_g for the orthorhombic phase of InVO_4 and the wolframite phase of InNbO_4 and InTaO_4 . We also present and discuss the effects of pressure on E_g . In particular, we report evidence of a band-gap collapse, at the structural transition pressure, for the three compounds as well as the pressure dependence of E_g for the low-pressure (LP) and HP phases. These studies have enabled us to improve the understanding of the physical properties of InVO_4 , InNbO_4 , and InTaO_4 and their behavior under compression. The combination of new experimental techniques, like transport measurements, and the systematic discussion of the three compounds has allowed us a fully consistent picture for the three compounds, solving the apparent discrepancies above described. The obtained results will contribute to the optimization of technological applications [7, 8].

The paper is organized as follows. In Sect. 2, we describe the experimental and computational techniques. The results of the absorption and resistivity measurements as well as band structure calculations for the low- and high-pressure phases of the different compounds are presented and discussed in Sect. 3. Finally, a summary of the work and the conclusions are presented in Sect. 4.

2 Materials and methods

2.1 Experimental details

For the experiments, we have used polycrystalline samples synthesized by a ceramic route following the method reported in previous works [11, 12, 14]. The composition and purity of the samples were confirmed by energy-dispersive x-ray spectroscopy using a transmission-electron microscope operated at 200 keV. The crystal structure was verified by powder x-ray diffraction measurements (Cu K_α radiation). These results have been previously published [11, 12, 14].

Optical absorption measurements were performed using 10- μm -thick polycrystalline pellets, with parallel faces, made by compressing the synthesized powdered samples to 1 GPa between two tungsten carbide Bridgman anvils using a hydraulic press [28]. Absorption measurements in the visible—near-infrared range were made with the optical setup described in previous studies devoted to determine the optical absorption of wide band-gap semiconductors [29]. The absorption spectrum of each material was determined from the transmittance spectra measured using the sample-in, sample-out method [30, 31]. For HP

experiments, the samples were loaded in a diamond-anvil cell (DAC) with diamond anvils of culet size of 400 μm . We used an inconel gasket, pre-indented to a thickness of 50 μm with a 120- μm -diameter hole. The loading was performed carefully to avoid sample bridging between the anvils [32, 33]. Small ruby chips were used for pressure determination [34], and 16:3:1 methanol–ethanol–water mixture was used as pressure-transmitting medium [35].

Electrical resistance measurements under pressure up to 10 GPa were carried out using an opposed Bridgman-anvil setup [36] consisting of a 12-mm-face-diameter tungsten carbide anvil pair. A pair of pyrophyllite gasket of thickness 200 μm each with a central hole of 3 mm in diameter was used to contain the sample. Bismuth was employed for the pressure calibration [37] along with steatite as pressure-transmitting medium. A well-compacted and sintered powdered sample of 2 mm $\times$ 1.5 mm $\times$ 0.1 mm in dimension was utilized for the electrical resistance measurements. The ultra-low current measurements were performed at each value of pressure after a 2 min of pressure soaking time with a Keithley electrometer.

2.2 Calculation details

Band structure calculations are required to provide a rational explanation to the results from optical absorption experiments. We have already performed such calculations for InVO_4 [17] and InTaO_4 [11]. The simulations were carried out in the frame of density-functional theory (DFT) [38] with the Vienna ab initio simulation package (VASP) [39] and have been used here to discuss the experimental results. In the present work, similar calculations have been carried out for InNbO_4 . The pseudopotential projected augmented-wave method [40, 41] representing the all-electron charge density in the core region was employed. To accomplish an accurate description of InNbO_4 , the basis set of plane waves was extended up to an energy cutoff of 520 eV. The exchange-correlation energy was described by means of the generalized-gradient approximation (GGA) with the Perdew–Burke–Ernzerhof for solids (PBEsol) functional [42]. In addition, the Monkhorst–Pack scheme [43] was employed to generate a dense special k-point sampling for the Brillouin zone (BZ) integration ($6 \times 6 \times 6$ grid). The achieved convergence in the total energy was less than 1 meV per formula unit. The forces on the atoms were lower than 0.005 eV/ $\text{\AA}$, and the deviations of the stress tensor from a diagonal hydrostatic form were smaller than 0.1 GPa. It has been previously shown that for the three studied compounds, DFT calculations provide a good description of the crystal structure at different pressures [11, 12, 17]. Using the calculated crystal structures, electronic band structure calculations, at several pressures, were performed for InNbO_4 within the first Brillouin zone

along the high-symmetry direction Γ -Z-D-B- Γ -A-E-Z-C₂-Y₂- Γ , for the low- and high-pressure structures.

3 Results and discussion

3.1 Optical absorption and band structure at ambient pressure

The optical absorption coefficient (α) as a function of photon energy measured for the LP phase of InVO_4 and InNbO_4 is shown in Figs. 1 and 2, respectively. At ambient conditions, in both compounds, a steep absorption is observed, which corresponds to the fundamental absorption edge,

Fig. 1 (top) Absorption spectra measured at different pressures for the LP phase of InVO_4 . The dashed line is the fit to the ambient-pressure absorption spectrum using the model described in the text. The insets show E_g versus pressure. The symbols are the experimental results, and the dashed line is the linear fit to the experimental data. (bottom) Tauc plot used to determine E_g . The dashed line shows the extrapolation of the linear region to the abscissa

Fig. 2 (top) Absorption spectra measured at different pressures for the LP phase of InNbO_4 . The dashed line is fit to the ambient-pressure absorption spectrum using the model described in the text. The insets show E_g versus pressure. The symbols are the experimental results, and the dashed line is the linear fit to experimental data. The band crossing is indicated. (bottom) Tauc plot used to determine E_g . The dashed line shows the extrapolation of the linear region to the abscissa

plus a low-energy absorption band. This absorption band is compatible with a typical Urbach tail [44, 45], which has been previously observed in InTaO_4 [11] and in many other ternary oxides belonging to the AMO_4 family [46, 47]. The nature of the low-energy tail has been the subject of considerable debate and is beyond the scope of this paper [48, 49]. In order to clarify the controversies of the band-gap values for the studied compounds and their nature at ambient conditions, the absorption spectra have been analyzed using the Tauc plot [50]. In InVO_4 , the absorption spectrum follows a linear behavior in the high-energy region when plotted as $(\alpha E)^2$ versus photon energy (E) (see the bottom panel of Fig. 1), suggesting that the compound is a direct band-gap semiconductor. This result agrees with our recent band structure calculations [17]. In the case of InNbO_4 , $\sqrt{\alpha E}$ follows a linear relation with E (see the bottom panel of Fig. 2). This fact suggests that the compound is an indirect band-gap semiconductor as InTaO_4 [11]. The value of E_g determined from the Tauc plots for the three compounds of interest is summarized in Table 1. The determined band gaps of InVO_4 , InNbO_4 , and InTaO_4 are 3.62(5), 3.63(5), and 3.79(5) eV, respectively. In the case of InVO_4 , the value of E_g is slightly larger but consistent with the value reported by Yan et al. ($E_g = 3.4$ eV) [23]. For InNbO_4 , the value of E_g is slightly smaller but consistent with the value reported by Lv et al. ($E_g = 3.83$ eV) [20]. In the case of InTaO_4 , our value of E_g is only 5% smaller than the value reported by Malingowski et al. ($E_g = 3.96$ eV) [51]. This confirms that the studied compounds are wide-gap semiconductors.

Previous [11, 25, 27] and present theoretical studies corroborate the conclusions extracted from the experimental results. Calculations support that InVO_4 is a direct band-gap material with the gap at the Y point of the BZ. The calculated values [25, 27] tend to overestimate E_g (see Table 1). However, it should be noted here that the value of E_g is very sensitive to the functionals selected for DFT calculations [25] and differences of up to 1 eV between measured and calculated band gaps are typical [25, 46]. In spite of the overestimation of the calculated E_g , DFT confirms that InVO_4 is a direct wide band-gap material and nicely

Table 1 Experimental and theoretical values of the band gaps (E_g) at ambient pressure

Compound	Experiment				Theory		
	Gap nature	E_g (eV)	E_u (eV)	References	k points	E_g (eV)	References
InVO_4	Direct	3.62(5)	0.0897(5)	This work	$Y \rightarrow Y$	4.76	[17]
						4.02	[25]
InNbO_4	Indirect	3.63(5)	0.1098(3)	This work	$Y \rightarrow \Gamma-B$	3.29	This work
InTaO_4	Indirect	3.79(5)	0.0897(5)	[11]	$Y \rightarrow \Gamma-B$	3.74	[11]

The Urbach energy (E_u) determined from the fits made for the ambient-pressure absorption spectra are also included. For the calculations, k points for the top of the valence band and the bottom of the conduction band are indicated

Fig. 3 Band structure of InNbO₄ at ambient pressure

describes the pressure dependence of E_g as explained in the latter section. One possible reason for the difference between the computed band gap and experimental value of E_g might be the contribution of electron excitonic effects [25]. In the case of InTaO₄, the agreement between experiments and calculations is not only qualitative but quantitative [11] (see Table 1). This material is an indirect wide band-gap material with the top of the valence band at the Y point of the BZ and bottom of the conduction band at a point in the Γ -B direction.

For InNbO₄, we have obtained qualitatively similar results. The band structure is shown in Fig. 3. As happens in InTaO₄, calculations found InNbO₄ to be an indirect gap material with the bottom (top) of the conduction (valence) band at the same points of the BZ. In the case of InNbO₄, calculations underestimate E_g by 0.3 eV. Therefore, the combination of experiments and calculations indicates that the small band gaps previously reported (1.9 eV for InVO₄, 2.5 eV for InNbO₄, and 2.6 eV for InTaO₄) [15, 16] are probably underestimated values. This could be caused by a wrong interpretation of the low-energy Urbach tail, which in the diffused reflectance measurements reported earlier was assumed to be the fundamental intrinsic absorption. The fact that the low-energy tail does change under compression, while the step edge we assigned to the fundamental absorption blueshifts; it is a confirmation that the low-energy absorption is not due to electronic transitions from the valence band to the conduction band.

From the calculations, we also obtained the density of states of InNbO₄, which is shown in Fig. 4. In the figure, it can be seen that O 2p states dominate the upper part of the valence bands and Nb 4d states dominate the lower conduction bands with a small contribution from O 2p and In 5s states. Thus, the orbital composition of the band structure near the Fermi level is qualitatively similar in InNbO₄, InTaO₄, and InVO₄, being the band gap determined as first approximation by the

Fig. 4 Total electronic density of states (solid black line) and partial electronic density of states (in colors as denoted in the inset) of InNbO₄ at ambient pressure

molecular electronic structure of the NbO₄³⁻, TaO₄³⁻, and NbO₄³⁻ ions in analogy with the behavior observed in other AMO₄ compounds [52]. This fact will determine the pressure evolution of the band gap as we will discuss in next section.

In order to provide more evidence supporting that the absorption spectrum of the different compound corresponds to a fundamental gap plus a low-energy Urbach tail, we have fit the experimental results using a model in which the fundamental absorption dominates the absorption coefficient above a critical energy (E_{crit}) and the Urbach tail dominates it below E_{crit} [53]. In this model, the absorption coefficient as a function of the photon energy is given by:

$$\alpha(E) = \begin{cases} A_1 e^{\frac{E-E_g}{E_u}} & h\nu \leq E_g + E_{crit} \\ A_2 (E - E_g)^n & h\nu \geq E_g + E_{crit} \end{cases}$$

where the parameters A_1 and A_2 are correlated by imposing continuity of the function $\alpha(E)$ and its derivative. These conditions also determine the critical energy (E_{crit}), below which the Urbach exponential absorption is assumed. In the equation, E_u is the Urbach energy and n is equal to 1/2 or 2 for direct or indirect transitions, respectively. Assuming the E_g values determined from the Tauc plots (see Table 1) and using an iterative procedure, we have fitted the ambient-pressure absorption spectra shown in Figs. 1 and 2(top). As it can be seen, the fits (dashed red lines) reproduce well the experimental results (solid black lines), confirming that assuming a direct band gap for InVO₄ plus an Urbach tail and an indirect band gap for InNbO₄ plus an Urbach tail is a reasonable hypothesis to describe the absorption spectra of both compounds. From the fits, we have also determined E_u , which is also related to the

steepness parameter of the absorption tail. The obtained values are summarized in Table 1. They are comparable with the values obtained in related ternary oxides [44, 53].

3.2 High-pressure behavior of the band gap

In Figs. 1, 2, 5, and 6, we show optical absorption spectra at selected pressures for the low-pressure orthorhombic phase of InVO_4 and wolframite phase of InNbO_4 . The maximum pressure represented for each compound, i.e., 6.3 GPa in InVO_4 and 11 GPa in InNbO_4 , is just below the transition pressure in each compound. In both materials, we have observed a blueshift in the absorption spectra under compression, similar to the one reported for the

Fig. 5 (top) Absorption spectra measured at different pressures for the HP phase of InVO_4 . The dashed line is the fit to the 6.5 GPa absorption spectrum using the model described in the text. The insets show E_g versus pressure. The band-gap collapse is indicated. The symbols are the experimental results, and the dashed line is the linear fit to them. (bottom) Tauc plot used to determine E_g . The dashed line shows the extrapolation of the linear region to the abscissa

Fig. 6 (top) Absorption spectra measured at different pressures for the HP phase of InNbO_4 . The dashed line is the fit to the 11.5 GPa absorption spectrum using the model described in the text. The insets show E_g versus pressure. The band-gap collapse is indicated. The symbols are the experimental results, and the dashed line is the linear fit to them. (bottom) Tauc plot used to determine E_g . The dashed line shows the extrapolation of the linear region to the abscissa

low-pressure wolframite phase of InTaO_4 [11]. Following the same procedure that we used with the ambient-pressure absorption spectra, we have determined E_g for different pressures. The results are shown in the inset of Figs. 1 and 2. The behavior of E_g in InVO_4 is linear with pressure. E_g moves at a rate of $dE_g/dP = 13.3(5)$ meV/GPa. This value is comparable with the pressure coefficient obtained from calculations, $dE_g/dP = 8.9$ meV/GPa [17]. The opening of the band gap is caused by the fact that the conduction bands move toward higher energy faster than the valence bands which are less sensitive to pressure. The same phenomenon induces the blueshift of the band gap in InNbO_4 (see Fig. 2) and InTaO_4 [11]. However, these

two compounds have a slightly different behavior, with a kink in the pressure dependence of E_g near 6.5 GPa (see Fig. 2). In InNbO_4 , E_g moves at a rate of 26.8(1.1) meV/GPa up to a pressure of 6.6 GPa. After this pressure, the pressure dependence of E_g slows down to 10.4(2) meV/GPa. According to our band structure calculations, this feature is due to a band crossing. This is caused by the fact that there is a relative maximum in the valence band at the Z point of the BZ which moves faster toward higher energies than absolute maximum of the valence band located at the Y point at ambient pressure. As a consequence, the Z point becomes the absolute maximum beyond 6 GPa. The different pressure dependence of both maxima not only drives the band crossing but also cause the change on the pressure dependence of E_g that we commented when describing the experiments.

The band-crossing phenomenon discovered near 6.5 GPa in InNbO_4 has been observed for InTaO_4 at a similar pressure ($P \sim 7$ GPa) [11] and is typical of wolframite-type compounds [10]. For instance, it has been found in CdWO_4 around 5 GPa [54] and it is a consequence of the non-isotropic compressibility of wolframite and the distortion induced by pressure in the TaO_6 (NbO_6) octahedron. In contrast, the VO_4 tetrahedron is much less compressible than these units, resulting in the lesser sensitivity of the band structure topology with pressure.

Increasing the pressure beyond 6.3 GPa (11 GPa) in InVO_4 (InNbO_4), we observed a color change in the samples from colorless to yellow. This color change is due to a band-gap collapse which can be clearly seen by comparing Figs. 1 and 2 with Figs. 5 and 6. The pressure where the abrupt collapse of the band-gap is observed is consistent with the structural phase transition found by XRD and Raman experiments in both compounds [12, 14]. The same band-gap collapse has been detected in InTaO_4 at the phase transition near 13 GPa [11]. A similar analysis as for the LP phase has been done for the HP phase to study its band-gap nature and value. We found that the absorption spectrum of both compounds follows a linear

behavior in the high-energy region when is plotted as $(\alpha E)^2$ versus photon energy (E) (see Fig. 5 and 6 bottom panel), suggesting that in the HP phase, both compounds are direct band-gap semiconductors. To corroborate these findings, we used the model employed for the absorption coefficient of the low-pressure phase to fit the absorption spectra of the HP phase assuming a direct band gap. As it can be seen in Fig. 5 and 6, the experimental data and the adjusted model are in good agreement in both the compounds. The values obtained for E_g in the HP phase are given in Table 2. There it can be seen that in the three compounds, there is a band-gap collapse, being the band gap considerably smaller in the HP phase than in the LP phase. In addition, after the phase transition, we noticed an increase in the Urbach energy which becomes approximately 0.130(5) eV for the HP phase of the three compounds, which suggest an increase in the crystal lattice disorder.

In the inset of Figs. 5 and 6, we show the pressure dependence of E_g . In both insets, the band-gap collapse is quite evident. It can also be seen that the band gap follows a linear behavior with pressure in the HP phase. However, there is a difference between both compounds. In InVO_4 , after the transition, E_g increases with pressure. This is consistent with the fact that the HP phase of InVO_4 is isostructural to the low-pressure phase of InNbO_4 and InTaO_4 , so a blueshift is expected for the HP phase of InVO_4 as happen in the LP phase of the other two compounds. In contrast, in the HP phase of InNbO_4 , the band gap redshifts under compression, exactly as happened in InTaO_4 . From the measurements made up to the maximum pressure reached in the experiments, 16 GPa for InVO_4 and 20 GPa for InNbO_4 , we determined dE_g/dP about 8.5(3) meV/GPa in the case of InVO_4 and $-9.6(2)$ meV/GPa in the case of InNbO_4 , which is very similar to the pressure coefficient of $-8.0(3)$ eV reported for InTaO_4 . All these results are summarized in Table 2.

Before discussing the calculations carried out for the HP phases, we would like to remark the fact that in the three

Table 2 Experimental and theoretical values of the band gaps (E_g) of the HP phase and pressure coefficient for the LP and HP phases

Compound	Study type	dE_g/dP (meV/GPa) (LP)	dE_g/dP (meV/GPa) (LP BC)	Gap nature (HP)	E_g (eV)	ΔE_g collapse (eV)	dE_g/dP (meV/GPa) (HP)	References
InVO_4	Exp.	13.3(5)		Direct	2.20(5)	1.51(10)	8.5(3)	This work [17]
	Theo.	8.9		Direct	3.06	1.77	9.3	
InNbO_4	Exp.	26.8(1.1)	10.4(2)	Direct	2.70(5)	1.20(10)	$-9.6(2)$	This work
	Theo.	14.8	5.0	Direct	2.02	1.45	-5.1	
InTaO_4	Exp.	20.1(9)	15.1(9)	Direct	2.70(5)	1.3(10)	$-8.0(3)$	[11]
	Theo.	19.8	16.4	Direct	2.25	1.61	-3.9	

The letters BC refer to the low-pressure phase of InNbO_4 and InTaO_4 for pressures after the band crossing and before the phase transition. The band-gap collapse at the phase transition (ΔE_g) is also given

Fig. 7 Band structure of HP InNbO₄ at 16.3 GPa

HP phases, the band gap is in the range $2.2 \text{ eV} < E_g < 2.7 \text{ eV}$, which makes these phases more suitable than the LP phases for photocatalytic water splitting [55]. Given the possibility of synthesizing the HP polymorphs of InNbO₄, InTaO₄, and InVO₄ as metastable phases at ambient conditions, by means of soft-chemistry methods [56] or using a large-volume apparatus [57], it would be possible in the immediate future to test their photocatalytic properties with the aim of using them in technological applications. Such studies are beyond the scope of this work.

We will now comment in more detail on the calculated band structure of the HP phase of InNbO₄ which is shown in Fig. 7. By comparing it with the band structure of the low-pressure phase, it can be noticed that the band structure of the HP phase is much more dispersive than the one of the LP phase. In addition, it resembles very much the band structure of the HP phase of InTaO₄ [11]. On the other hand, the calculations indicate that the HP phase of InNbO₄ is a direct gap semiconductor (as the one of InTaO₄). The maximum of the valence band and the minimum of the conduction band are located at the Γ point of the BZ. This result is in agreement with the conclusion extracted from the analysis of absorption spectra of the HP phase. The theoretical value of E_g at 16.3 GPa is 2.02 eV. This value is 0.7 eV smaller than the measured E_g , being the difference within the range of the typical differences between DFT calculations and experiments. In spite of it, calculations confirm that there is large band-gap collapse at the phase transition in InNbO₄ as it also happens in InTaO₄. In addition, calculations give a similar evolution of E_g with pressure than the experiments. Specially, they confirm the redshift of the band gap of the HP phase under compression, which is different than the behavior of the LP phases of InVO₄, InNbO₄, and InTaO₄, and the HP phase of InVO₄ in which the band gap blueshift under compression.

As happen in the HP phase of InTaO₄, the band gap of the HP phase of InNbO₄ redshifts because the top of the valence band moves faster toward higher energies than

Fig. 8 Total electronic density of states (solid black line) and partial electronic density of states (in colors as denoted in the inset) of HP InNbO₄ at 16.3 GPa

the bottom of the conduction band. This phenomenon can be understood by taking a look to the electronic density of states which is shown in Fig. 8. The main qualitative difference of it with the LP phase is the contribution of In 4d states to the top of the valence band. These states shift with pressure in direction of higher energies faster than O 2p and Nb 4d states, and therefore, the top of the valence band shifts to higher energies faster than the bottom of the conduction band, causing the observed small redshift of E_g . The role of In 4d states is analogous to the role of Mn 3d states in wolframite-type MnWO₄ [58], in which the band gap closes under compression as opposed to the behavior of other wolframite like CdWO₄, ZnWO₄ and MgWO₄.

3.3 Resistivity measurements

Resistivity measurements were carried out up to 10 GPa on all the compounds studied in this work including InTaO₄. The results obtained from the experiments are shown in Fig. 9. As can be seen there, all the compounds at room conditions present a large resistivity of the order of M Ω .cm. These resistivity values suggest that the charge transport cannot be caused by the thermal activation of electrons from the valence band to the conduction band. At ambient conditions (1 bar and 300 K), the thermal energy (the product of the Boltzmann constant and the temperature) available to promote electrons from the valence to the conduction band is 25 meV. Thus, in our compounds, due to their wide band-gap energy ($E_g > 3.62 \text{ eV}$), the thermal energy is approximately $1/150 E_g$. Therefore, the intrinsic density of free electrons in the conduction band is negligible. As a consequence, the wide band-gap semiconductors InNbO₄, InTaO₄, and InVO₄ cannot be in the intrinsic regime [59]. Notice that even in a narrow-gap semiconductor like

Fig. 9 Resistivity as a function of pressure measured for the three studied compounds. The compounds are identified in the inset

GaAs, the intrinsic resistivity is of the order of $108 \Omega \cdot \text{cm}$ [60], i.e., two orders of magnitude larger than in InVO_4 , InNbO_4 , and InTaO_4 .

In a recent work by R. van de Krol et al. [58], it has been determined for thin films of InVO_4 an electrical conductivity of $\sim 4 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$ (resistivity $\sim 25 \times 10^6 \Omega \text{cm}$) which is consistent with our result at ambient conditions of $13.0(5) \times 10^6 \Omega \text{cm}$ for such compound. Also, at room temperature, the carrier concentration is estimated to be 10^{11}cm^{-3} . Then, assuming an electron mobility of $10 \text{cm}^2/(\text{Vs})$ typical of polycrystalline materials [61] (like our samples), it will lead a resistivity of the order of $10 \text{M}\Omega \text{cm}$ as measured. The electrical conductivity on InVO_4 has been attributed to the presence of donor states at $\sim 0.7 \text{eV}$ below the conduction band [62]. The presence of these donor states has been related mainly to deviations from the ideal In:V ratio of 1:1. Notice that a deviation of 0.05% corresponds to a donor density of approximately $6 \times 10^{19} \text{cm}^{-3}$. The low bulk conductivity is because only a small fraction of these donors will be ionized [62].

Under compression up to nearly 1.6 GPa, the resistivity increases with pressure in the three compounds. If we assumed that the electron mobility is not affected by pressure up to 1.6 GPa, from the pressure dependence of the resistivity, the pressure evolution of the activation energy of donor states has been calculated to be 8.9(8), 2.5(3), and 4.5(2) meV/GPa for InVO_4 , InNbO_4 and InTaO_4 , respectively. In all the cases, the activation energy increases as pressure increases in order to explain the behavior of the resistivity. This is consistent with the widening of the band-gap under pressure which will favor the increase in the effective mass of the electrons in the conduction band, making the donor states to move further away from the bottom of the conduction band [63].

At the pressure of about $\sim 1.6 \text{GPa}$, the resistivity of InVO_4 shows a sharp discontinuity. This discontinuity in the resistivity can be attributed to the structural phase transition and the collapse of the band-gap that the compound experiences under quasi-hydrostatic conditions at 6.3 GPa. The reduction in the transition pressure in the resistivity measurements is related to the fact that these experiments have been performed under non-hydrostatic conditions, which usually induces a lowering of the transition pressure [63–66], in some cases up to 10 GPa [67, 68]. From 1.6 GPa to the maximum pressure achieved in the experiments, the resistivity of InVO_4 follows a smooth behavior which is consistent with the fact that a second-phase transition in InVO_4 is only expected to occur at 28 GPa [17].

We will comment now the results on the other two compounds. Near 1.6 GPa, InNbO_4 and InTaO_4 present a kink in the pressure dependence of the resistivity, which could be presumably associated with the band crossing that it has been observed near 6.5 GPa in both materials. The phenomenon is more evident in InNbO_4 than in InTaO_4 . In particular, the band crossing might lead to a reduction in the activation energy of donors, leading to an increase in the carrier concentration which necessarily will be reflected in the pressure dependence of the resistivity. However, the observed behavior could be caused by many other factors like a change of the carrier mobility. To clarify this issue, measurement as a function of temperature at different pressures should be performed, which is beyond the scope of this work.

In InNbO_4 , a discontinuity has been observed in the resistivity at 9.5 GPa which evidences the existence of the phase transition. In contrary to InTaO_4 , no discontinuity has been observed up to 10 GPa. The detection of the transition in InNbO_4 at 9.5 GPa and not at 11 GPa is related with the presence of non-hydrostatic stresses in the resistivity experiments, as we already discussed for the reduction in the transition pressure in InVO_4 . In InTaO_4 , the transition occurs at 13 GPa and therefore is not surprising that it is not detected in the resistivity measurements (maximum pressure 10 GPa). One hypothesis to explain the increase in the resistivity at the phase transition in InNbO_4 is the generation of defects. Indeed, as commented before, we have observed that the Urbach energy increases considerably after the phase transition in InNbO_4 . This supports the hypothetical formation of defects at the transition. The defects can act as recombination centers, reducing the carrier concentration and leading to the observed increase in the resistivity.

4 Conclusions

By means of the combination of optical absorption measurements and band structure calculations, we have shown that InVO_4 , InNbO_4 , and InTaO_4 are wide band-gap

materials with energy band gaps of 3.62(5), 3.63(5), and 3.79(5) eV, respectively. We have also determined the pressure dependence of the band-gap energy up to nearly 20 GPa. In the low-pressure phase of the three compounds, the band gap blueshifts under compression. In all of them, we have also observed a band-gap collapse that can be correlated with the previously observed phase transitions. Band structure calculations provide a rational explanation to the observed behaviors. In particular, a picture that satisfactorily explains the electronic properties at ambient and high pressure has been proposed. Finally, resistivity measurements are consistent with the optical experiments. They have been useful to determine that the three materials are not intrinsic semiconductors. Possible reasons for the behavior of the resistivity have been discussed. We consider the reported results a contribution to deepen the understanding of the electronic properties of the photocatalytic materials InVO_4 , InNbO_4 , and InTaO_4 . The accurate determination of band-gap energies and the consistence between different experimental techniques and computer simulations make our findings relevant for the optimization of applications like photocatalytic production of hydrogen from water splitting.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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