

RESEARCH OUTPUTS / RÉSULTATS DE RECHERCHE

Elucidations of electronic and optical properties of the w-ZnCh (Ch=O, S and Se) compounds

Halati, Mohamed Salah; Lounis, Zakia; Khyzhun, Oleg Y.; Caudano, Yves; Shoush, Kamel A.; Paramasivam, Prabhu; Ghoneim, Sherif S.M.

Published in:
IET Optoelectronics

DOI:
[10.1049/ote2.12128](https://doi.org/10.1049/ote2.12128)

Publication date:
2024

Document Version
Publisher's PDF, also known as Version of record

[Link to publication](#)

Citation for pulished version (HARVARD):

Halati, MS, Lounis, Z, Khyzhun, OY, Caudano, Y, Shoush, KA, Paramasivam, P & Ghoneim, SSM 2024, 'Elucidations of electronic and optical properties of the w-ZnCh (Ch=O, S and Se) compounds: Insights from Ab-initio calculations and spectroscopy measurements', *IET Optoelectronics*, vol. 18, no. 6, pp. 188-218.
<https://doi.org/10.1049/ote2.12128>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal ?

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

ORIGINAL RESEARCH

Elucidations of electronic and optical properties of the w-ZnCh (Ch=O, S and Se) compounds: Insights from Ab-initio calculations and spectroscopy measurements

Mohamed Salah Halati^{1,2,3} | Zakia Lounis¹ | Oleg Y. Khyzhun^{4,5} | Yves Caudano⁶ | Kamel A. Shoush⁷ | Prabhu Paramasivam^{8,9}  | Sherif S. M. Ghoneim⁷

¹Laboratory of Materials (LABMAT), National Polytechnique School (ENP) of Oran, Oran, Algeria

²Scientific and Technical Research Centre for Arid Areas C.R.S.T.R.A Omar El Barnaoui, Campus of Mohamed, Khider University of Biskra, Biskra, Algeria

³Research Center in Industrial Technologies(CRTI), Additive Manufacturing Research Unit (URFA), Setif, Algeria

⁴Frantsevych Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, Kyiv, Ukraine

⁵Jan Dlugosz University in Częstochowa, Częstochowa, Poland

⁶Research Unit Lasers and Spectroscopies (UR-LLS), naXys & NISM, University of Namur, Namur, Belgium

⁷Department of Electrical Engineering, College of Engineering, Taif University, Taif, Saudi Arabia

⁸Department of Research and Innovation, Saveetha School of Engineering, SIMATS, Chennai, Tamil Nadu, India

⁹Department of Mechanical Engineering, Mattu University, Mettu, Ethiopia

Correspondence

Mohamed Salah Halati and Prabhu Paramasivam.

Email: mohamedsalah.halati@yahoo.fr and prabhu.paramasivam@meu.edu.et

Funding information

Taif University, Grant/Award Number: TU-DSPP-2024-14

Abstract

The electronic and optical properties of IIB-VIA Zn-based monochalcogenides w-ZnCh (Ch: O, S and Se) were reported. The band structures using the FP-LAPW method at zero pressure with the Tran–Blaha-modified Becke–Johnson potential evidence that w-ZnO, w-ZnS and w-ZnSe reveal direct band gaps (Γ – Γ) of 2.72, 3.87, and 2.88 eV, respectively. The complex dielectric function $\epsilon(\omega)$, refractive index $n(\omega)$, extinction coefficient $k(\omega)$, absorption coefficient $\alpha(\omega)$, reflectivity $R(\omega)$, energy-loss function $L(\omega)$ and complex conductivity $\sigma(\omega)$, are determined. The microscopic origin of the observed fine-structure peculiarities in the spectra of the imaginary part of the dielectric function ($\epsilon_2(\omega)$) is identified. An intensive X-Ray PhotoElectron Spectroscopy (XPES) investigation shows the effect of controlled UHV treatment (Ar^+ ionic bombardment followed by gradual heating) as a method of cleaning and/or re-crystallising the upper layers. XPES and XAES (Auger Electron induced by X-Ray Excitation) transitions substantiate successfully the UHV in situ cleaning. The valence band structure was studied. The PLS technique employing UVvis excitation source of a 325 nm (He–Cd) gas laser unveils that ZnO, zinc sulfide and ZnSe luminescence mechanism concerns the energy band gap. The results of the experimental studies are found to be in good agreement with the theoretical predictions.

KEYWORDS

laser beams, laser modes

All authors have contributed equally in the preparation of this manuscript.

This is an open access article under the terms of the [Creative Commons Attribution](https://creativecommons.org/licenses/by/4.0/) License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2024 The Author(s). *IET Optoelectronics* published by John Wiley & Sons Ltd on behalf of The Institution of Engineering and Technology.

1 | INTRODUCTION

Theoretical and experimental studies of $\text{II}_\text{B}\text{-VI}_\text{A}$ zinc-based mono-chalcogenide semiconductors ZnCh (Ch : O, S and Se) constitute a very active research area [1–5] due to their interesting useful properties which make them the target of many present works. In fact, ZnCh (Ch : O, S and Se) are promising materials in various technological fields. There are current interests to show their efficient role in the development of both sound acoustic wave filters in the new sixth-generation (6G) mobiles and in wireless communications platforms [6], valuable materials in industrial additive manufacturing [7], highly sensitive underwater acoustic sensors [8], internet of things [9], cholesterol sensing [10], coating layers on 2D graphene substrates [11, 12], bio-sensors [4, 13], high-density optical memories [14], hydrogen storage devices [15], antibacterial activities etc. [16, 17].

The current study is focused on the electronic and optical properties of the wurtzite-type ZnCh (Ch : O, S and Se) compounds (w- ZnCh). The wurtzite-type structure is the main one of the monochalcogenides which can be easily synthesised at appropriate laboratory conditions [18–22]. For this purpose, rigorous theoretical calculations unified with powerful experimental techniques were employed to explore in-depth the electronic and optical properties of the $\text{II}_\text{B}\text{-VI}_\text{A}$ mono chalcogenide w- ZnCh (Ch : O, S and Se) compounds. Blaha et al. [23] suggest that, nowadays, the theoretical calculations performed within a framework of density functional theory (DFT) rival or even surpass the accuracy of experimental results for predictions of ground state properties of materials at the zero pressure condition. The present theoretical study was performed employing the state-of-the-art full-potential (linearised) augmented plane wave (FP-LAPW) method with the Tran–Blaha-modified Becke–Johnson potential (TB-mBJ) [23–26]. This technique has proved its merit for predicting the physicochemical properties of a large variety of materials [25]. With respect to UHV experimental studies, the XPES (X-Ray Photo Electron Spectroscopy) [27], REELS (Reflective Electron Energy Loss Spectroscopy) [28], PLS (Photoluminescence Spectroscopy) [29] and UVS (Ultraviolet visible spectroscopy) [30] techniques were employed to analyse the electronic and optical properties of the titled materials.

The present theoretical results are found to be in excellent agreement with the experimental measurements and available literature data [1–4, 18].

2 | THEORETICAL STUDY

2.1 | Computational approach and setting

The FP-LAPW approach within the DFT framework is incorporated in the modern WIEN2k package (21.1 version) [31]. The Tran–Blaha-modified Beck–Johnson (TB-mBJ) potential [23–26] was used in the present work to treat the exchange-correlation (XC) potential in all the quantum

mechanics calculations. The FP-LAPW method within the TB potential has proven its effectiveness in predicting the electronic structure and associated properties of materials providing comparatively low computational-time cost. In the FP-LAPW formalism, the crystal unit cell is divided into non-overlapping muffin tin spheres (MTS) surrounding each atom, separated by an interfacial region (IR). The MTS radii are chosen as large as possible without overlapping. The Kohn–Sham wave functions inside the MTS are developed in spherical harmonics, while in the IR, they are developed in a plane wave basis set truncated at a reciprocal lattice vector K_max . The chosen computational settings are as follows: the MTS radii are 1.93, 1.66, 1.86, and 2.24 Bohr for Zn, O, S and Se, respectively. The highest angular moment for the spherical harmonics basis set $l_\text{max} = 10$; $K_\text{max} = 8/R_\text{MT}^\text{min}$, where R_MT^min is the smallest muffin-tin sphere. Integration over the Brillouin zone (BZ) was performed using a $40 \times 40 \times 21$ Monkhorst-Pack grid [32].

2.2 | Electronic properties

2.2.1 | The calculated electronic band structure:

To the best of our knowledge, high precision studies of the electronic structure of ZnCh (Ch : O, S and Se) compounds need to employ an exchange and correlation (E_XC) potential that give the closest output to the experimental measurements. In fact, the TB-mBJ model is regarded suitable for our case. Figure 1 presents the calculated electronic band structures along the paths defined by high symmetry points in the Brillouin zone (BZ; Figure 2-Right) for ZnO, zinc sulfide (ZnS) and ZnSe within the hexagonal closed packed (hcp) cell as shown in Figure 2-Left, at their equilibrium structural parameters using the TB-mBJ potential in the present calculations. So, for all considered compounds, the valence band maximum (VBM^ax) and the conduction band minimum (CBM^in) are located at the BZ centre (Γ -point). The calculated fundamental optical band gap ($E_g^{\Gamma-\Gamma}$) is equal to 2.72 eV for ZnO, 3.87 eV for ZnS and 2.88 eV for ZnSe. Figure 3 provides a comparison between our predicted band gap values and the available experimental [1–4, 33, 34] and numbers of previous theoretical calculations [18, 19], using various approaches for E_XC potential. First of all, it is noted that the values of the band gaps previously calculated for ZnCh employing the commonly used GGA and LDA approximations are remarkably underestimated as compared to the available experimental data. The underestimation is about -40% to -50% in such a case. Second, the predicted $E_g^{\Gamma-\Gamma}$ values using the TB potential are close to those of the related experimental data. The deviation of the calculated band gap compared to the corresponding measured one is less than $(+20.93\%, +9.32\%$ and $+4.44\%)$ for ZnO, ZnS and ZnSe, respectively, proving the reliability of the used theoretical model. Note that the energy bands around the CBM^in are more dispersive than those around the VBM^ax ,

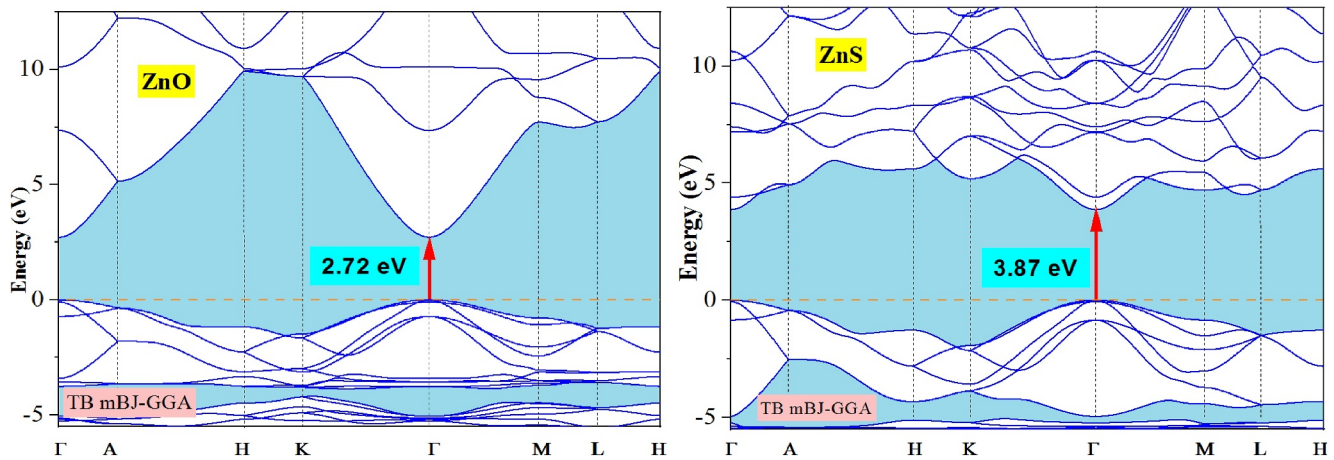


FIGURE 1 Calculated electronic band structures of the w-(ZnO, ZnS and ZnSe) compounds. The fundamental band gap is shown by a red arrow. The Brillouin zone of the hexagonal *ZnCh* with the high symmetry axes. See ref [5] for w-ZnSe compound.

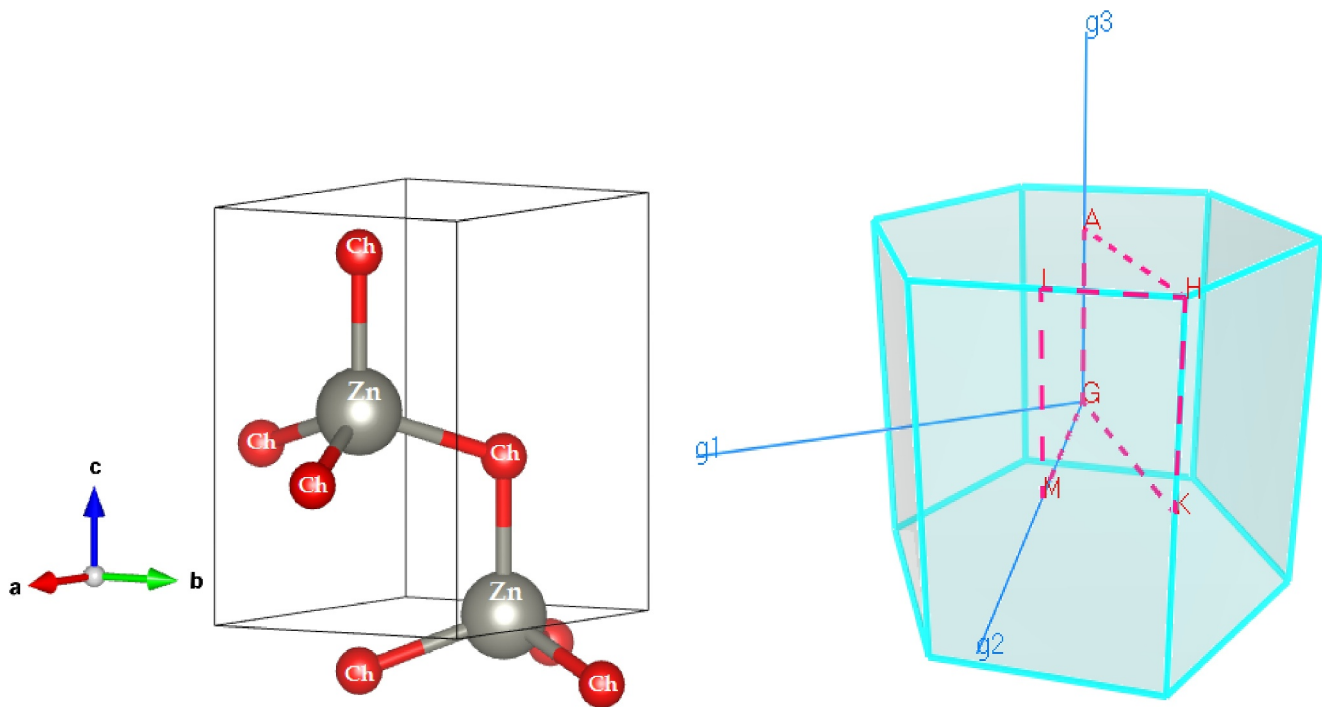


FIGURE 2 (Left) w-ZnCh crystal structure. Red atoms (Chalcogens: O, S and Se) and grey atoms present Zn ones (right) the 3D reciprocal space- 1st Brillouin zone along the lines of high symmetry: $G \rightarrow A \rightarrow H \rightarrow K \rightarrow G \rightarrow M \rightarrow L \rightarrow H$.

indicating that the holes are heavier than electrons in the titled compounds.

2.2.2 | Charge carrier effective masses (electrons and holes)

The effective masses of charge carriers are the key fundamental quantities governing the transport properties in materials and for verifying the reliability of experimental and theoretical models for certain physical phenomena. The charge carrier effective mass is generally a tensor, but it can be treated as

scalar at the energy band extrema. So the effective mass m_* can be calculated from the second order derivative of the energy dispersion $E(\vec{k})$ as follows:

$$(m^*)^{-1} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2} \quad (1)$$

The calculated electron effective mass (m_e^*), heavy and light hole effective masses (m_{hh}^* and m_{lh}^*), respectively, split-off hole (m_{sh}^*) and split-off energy (E_{so}) at the Γ -point towards both the M-point (perpendicular to the c -axis and thus

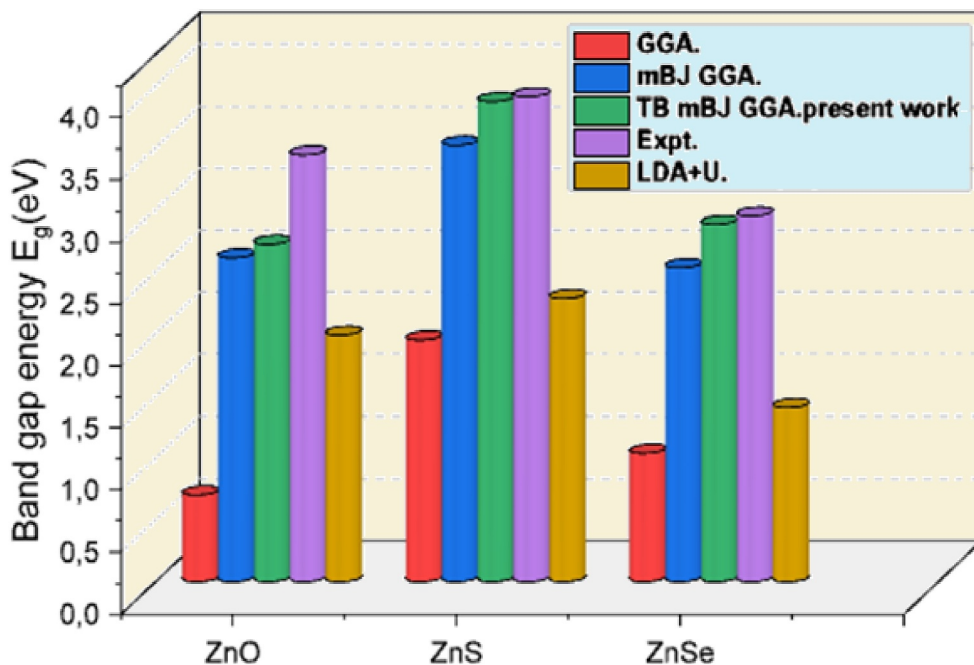


FIGURE 3 Comparison of the fundamental direct band gap ($E_g^{\Gamma-\Gamma}$) of $w\text{-Zn}Ch$ ($Ch=\text{O, S and Se}$) calculated using the FP-LAPW method via (TB-mBJ) functional, other calculations using different functional (GGA, LDA + U) [18] and the available experimental data [3, 41].

TABLE 1 Calculated effective masses of electrons and holes (in units of the free-electron mass m_0) for the $w\text{-Zn}Ch$ (Ch : O, S, Se) compounds. $m_e^{*\perp}$ and $m_e^{*\parallel}$ are electron effective masses at the CBM (Γ -point) towards M- and A-points, respectively. $m_{hh}^{*\perp}$ ($m_{hh}^{*\parallel}$) are heavy (light) effective masses at the VBM (Γ -point) towards M- and A-points, respectively. $m_{sh}^{*\perp}$ and $m_{sh}^{*\parallel}$ are split-off hole. E_{so} is the splitting-off energy (in meV). TB-mBJ: Present work; LDA, GGA, and LDA + U: Ref. [18]; Expt. Ref. [33, 34] for $w\text{-ZnO}$ and $w\text{-ZnS}$; Expt. Ref. [4] for $w\text{-ZnSe}$).

Compound	$m_e^{*\perp}$	$m_e^{*\parallel}$	$m_{hh}^{*\perp}$	$m_{hh}^{*\parallel}$	$m_{sh}^{*\perp}$	$m_{sh}^{*\parallel}$	$m_{sh}^{*\perp}$	$m_{sh}^{*\parallel}$	E_{so}
<i>w</i> -ZnO									
TB-mBJ	0.288	0.312	0.547	0.523	0.797	0.521	0.808	0.215	720.9
LDA	0.130	0.137	2.063	2.447	0.227	2.979	0.288	0.169	
GGA	0.143	0.144	0.351	2.266	0.300	3.227	0.537	0.165	
LDA + U	0.209	0.189	11.401	0.207	3.111	4.330	0.270	0.330	
Expt.	-	0.240	0.590	0.590	0.590	0.590	0.550	0.310	
<i>w</i> -ZnS									
TB-mBJ	0.253	0.284	0.623	1.362	0.271	0.212	0.310	0.163	827.3
LDA	0.153	0.144	3.838	1.746	0.180	0.756	0.337	0.183	
GGA	0.199	0.142	1.713	2.176	0.198	0.402	0.443	0.440	
LDA + U	0.157	0.138	2.194	1.785	0.195	0.621	0.303	0.339	
Expt.	-	0.280	0.490	1.400	-	-	-	-	
<i>w</i> -ZnSe									
TB-mBJ	0.215	0.184	2.160	1.730	0.276	0.187	0.288	0.451	764.7
LDA	0.139	0.148	0.158	1.404	0.124	0.114	0.197	0.171	
GGA	0.149	0.184	0.184	1.395	0.173	0.135	0.306	0.190	
LDA + U	0.149	0.185	0.189	1.629	0.187	0.137	0.344		
Expt.	0.170	0.170							

subscribed ($\perp$) and A-point (parallel to the c -axis; subscribed ($\parallel$)) are compiled in Table 1. It is apparent from Table 1 that the evaluated heavy holes along all directions and the light

holes along the perpendicular direction ($\perp$) are much heavier than the electrons along all directions reflecting the n-type of semiconductor mobility. Compared to holes, one can conclude

that the electrons are much more isotropic. The calculated effective masses for electrons and light holes using TB-mBJ approach are the closest to experimental values, while those of heavy hole are overestimated as compared to the experimental findings.

2.2.3 | Density of states

The nature identification of the fundamental electronic states in such a compound which populate the energy levels in their bands is closely related to the observable physico-chemical properties of materials. For this purpose, the total density of states TDOS and the atom-projected angular momentum (L) decomposed density of states PDOS of w-type ZnO, ZnS and ZnSe were calculated. The valence shells and electronic configurations for pseudo-atoms are: Zn: $4s^2 3d^{10}$, O: $2s^2 2p^4$, S: $3s^2 3p^4$ and Se: $4s^2 3d^{10} 4p^4$. It is obvious from Figure 4 that the valence band in each $ZnCh$ compound consists of three sub-bands labelled V1, V2 and V3. A good knowledge on the upper valence band (UVB), denoted V1, is helpful to explore the bonding characteristics.

The upper valence band width (UVBW) in ZnO is equal to 5.20 eV, while it increases by +16.5% in ZnS and +23.1% in ZnSe compared to that of ZnO, indicating that the ionic character of the chemical bonding increases in the sequence $ZnO \rightarrow ZnS \rightarrow ZnSe$. In ZnO, the subdivision in structure of the valence band V1 arises at about -3.8 eV, accompanied by very weak electronic contributions for both O and Zn species. Regarding ZnS (ZnSe), the UVB splitting clearly extends between -5.02 eV (-5.58 eV) and -4.75 eV (-4.57 eV) into the V_1 and V_2 bands, respectively. So, the splitting effect forms a pseudo-gap in the valence band region of w-ZnSe (nearly 1.01 eV), which is four times bigger than that of w-ZnS (0.27 eV).

We also want to note that the contribution input of Zn atoms changes as follows:

Zn- $3d$ electrons dominate in w-ZnO throughout the UVB, while in the valence band V1 of ZnS(ZnSe) Zn $3d$ states are found to appear together with S- $3p$ (Se- $4p$ and Se- $3d$) states which are more localised in such a case. Furthermore, smaller electronic contributions of Zn- $4s$ and Zn- $3p$ states in the valence band V1 of ZnS(ZnSe) are also detected in the present first-principles calculations of ZnS(ZnSe). However, in the

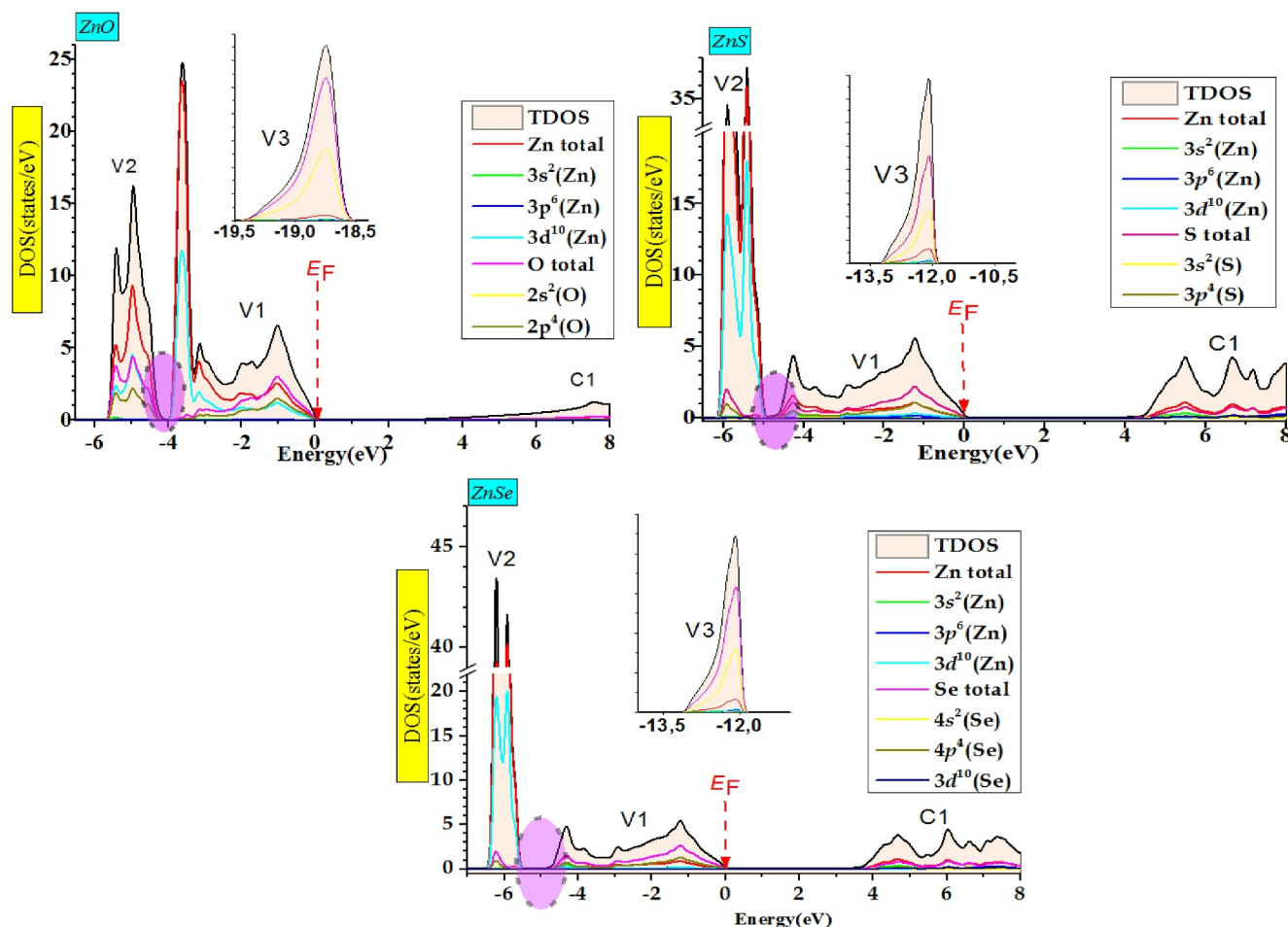


FIGURE 4 Calculated electronic density of states (EDOS) up to down, wurtzite (ZnO, ZnS and ZnSe), respectively.

valence band V2, contributions of Zn-3d states still dominate compared with those of chalcogen p states.

In order to support our statement, it is pertinent to consider the electro-negativity difference ($\Delta\chi$) values between the atoms composing the ZnCh compounds, which are equal to 1.79 (2.020), 0.93(0.999) and 0.90(0.834) for ZnO, ZnS and ZnSe, respectively, using the Pauling (Allen) scales [35, 36]. Pauling et al. [35] reported that for compounds possessing $\Delta\chi$ values smaller than 1.7, there exist chemical bonds with a dominating covalent component and a little amount of ionic ones.

The PDOS curves exhibit that the relative intensities of the sub-bands labelled V2 (a structure with two well resolved tops) increase in intensity in this sequence of ZnO to ZnS to ZnSe compound. Furthermore, we detect the formation of the well distinguished peaks (V3) with high intensity, positioned at -18.74 eV, -12.10 eV and -12.05 eV (see the enlarged views in Figure 4), where chalcogen ns-like states are the dominant contributors ($n = 2$ for O, $n = 3$ for S and $n = 4$ for Se) with smaller contributions of 3p and 4s states associated with zinc. The bottom of the conduction band (C1) is formed prevalently by hybridised unoccupied Zn-4s and (O, S and Se)-p states. The carriers originating from the CBMⁱⁿ reveal the key features responsible for formation of optoelectronic properties of the titled semiconductors which are presented in the next paragraphs.

2.3 | Optical parameters

To identify the linear response of a compound to an external electromagnetic radiation, the dielectric function could be used as an important optical parameter, which is related to the interaction of external photons (IR, visible and UV) and the electrons of the compound. Two contributions (intra and interband) exist, which are responsible for determining the optical constants. However, in the present work, the intraband transitions were neglected, because they are important only for metals first-principles calculations and should be omitted in semiconductors case. Frequency-dependent macroscopic linear optical constants of w-ZnCh (Ch: O, S and Se) compounds are determined for incident electromagnetic waves polarised perpendicularly and parallel to the *c*-axis in a wide energy window extending from 0 to 20 eV. The tensor of the complex dielectric function ($\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$) of materials crystallising in a hexagonal structure has two non-zero independent components, $\epsilon^{xx}(\omega)$ and $\epsilon^{zz}(\omega)$. The $\epsilon^{xx}(\omega)$ and $\epsilon^{zz}(\omega)$ components correspond to electromagnetic radiation with electrical field $\vec{E}$ polarised parallel to the *a*-axis (perpendicular to the *c*-axis) and *c*-axis, respectively. The components $\epsilon_2^{ij}(\omega)$ of $\epsilon_2(\omega)$, which describe the absorption of the incident radiation by a medium, are calculated by summing all individual contributions of the electronic transitions from occupied electronic states $(\vec{k}, n)$ to unoccupied electronic states $(\vec{k}', n')$, where n and n' are the indexes of the bands and $\vec{k}$ is the wave vector, using the following relationship [37]:

$$\epsilon_2^{ij}(\omega) = \frac{Ve^2}{2\pi\hbar m_0^2 \omega^2} \sum_{n,n'} \int d^3k \langle kn | P_i | kn' \rangle \times \langle kn' | P_j | kn \rangle f_{kn} (1 - f_{kn'}) \delta(E_{kn'} - E_{kn} - \hbar\omega) \quad (2)$$

where $|kn\rangle$ is the wave function of the electronic state $(\vec{k}, n)$ corresponding to the energy E_{kn} and $|kn'\rangle$ is the wave function of the electronic state $(\vec{k}', n')$ corresponding to the energy $E_{kn'}$, P_i ($i = x, y, z$) is the momentum operator, f_{kn} is the Fermi distribution corresponding to the energy level E_{kn} and $\delta(E_{kn'} - E_{kn} - \hbar\omega)$ is the Dirac delta function. Components of the dispersive part of the dielectric function, that is, $\epsilon_1^{xx}(\omega)$ and $\epsilon_1^{zz}(\omega)$ of $\epsilon_1(\omega)$, can be deduced from those of the imaginary part of the complex dielectric function through the Kramers–Kronig [38, 39] transformation. The calculated spectra of the components of $\epsilon_2(\omega)$, namely $\epsilon_2^{xx}(\omega)$ and $\epsilon_2^{yy}(\omega)$, for the titled compounds are depicted in Figure 5 along with the experimental data. The $\epsilon_2^{xx}(\omega)$ and $\epsilon_2^{yy}(\omega)$ spectra exhibit some peaks, labelled E_i ($i = 1, 2, 3, \dots$) and the peaks in the corresponding experimental spectra are labelled e_i ($i = 1, 2, 3, \dots$). It is found that the calculated E_i peaks coincide well with the corresponding e_i peaks in the experimental spectra, proving the reliability of the used theoretical method to determine the optical properties. In order to determine the microscopic origin of the E_i peaks, we started by determining all band pairs (n, n') that are involved in all electronic transitions by decomposing the $\epsilon_2(\omega)$ spectrum into the excitation states (viz. individual contributions of each direct allowed electronic transition) from the occupied valence state $(\vec{k}, n)$ to the unoccupied conduction state $(\vec{k}', n')$ ($(\vec{k}, n) \rightarrow (\vec{k}', n')$), which will be labelled $V_i \rightarrow C_j$ hereafter (see Figure 5) as done in numerous works [42–46].

The corresponding $\vec{k}$ vectors in $(\vec{k}, n) \rightarrow (\vec{k}', n')$ electronic transitions were obtained from the transition energy band dispersion along the band structure path: $E(k) = E_{C_i}(k) - E_{V_i}(k)$ which is dispersed along the band structure path (Figure 6). The fundamental absorption edge (threshold energy) E_0 due to the direct optical transitions between the top of the valence band and the bottom of the conduction ($V_1 \rightarrow C_1$ transition) occurs at 2.72 eV in w-ZnO, 3.87 eV in w-ZnS and 2.88 eV in w-ZnSe. Positions of the centre of the main structures (E_i) in the spectra of the components of the $\epsilon_2(\omega)$ components and the extended direct inter-band transitions giving the dominant contributions to the optical structures and their regions in the first irreducible BZ are summarised in Tables 2–7. The contribution percentage of such band to band electronic transitions is described as the ratio between the latter subpeak intensity and the relative intensity of the relevant structure E_i as follows:

$$P(\%) = \frac{I_{(V_i \rightarrow C_i)}}{I_{E_i}} \times 100 \quad (3)$$

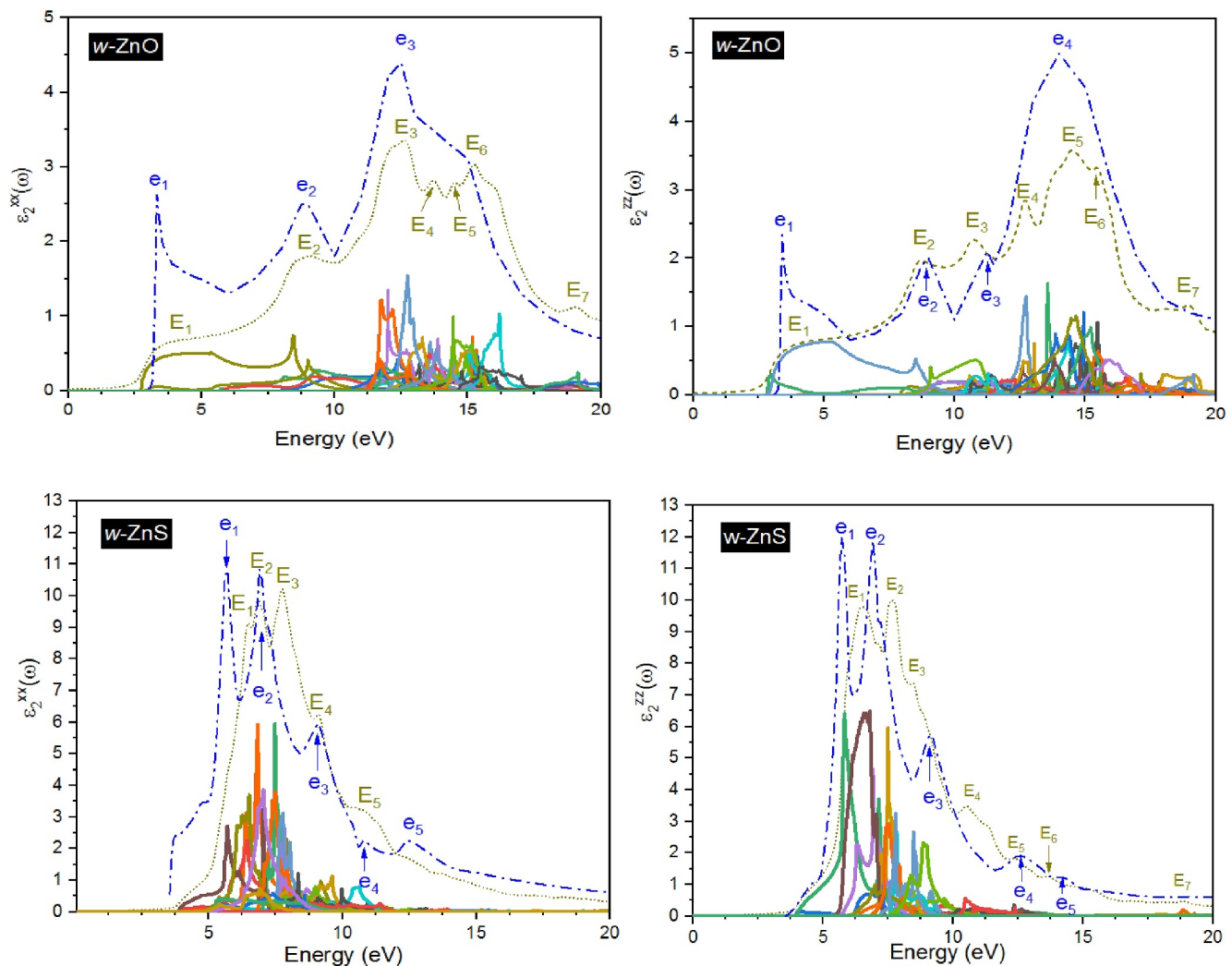


FIGURE 5 Decomposition of the components of the imaginary part of the dielectric function into band-to-band contributions. See Ref. [5] for w-ZnSe compound. Blue dashed line experimental results from [41].

Note that the principal contributions to the direct optical transitions originate from the UVB states to the bottom of the conduction band states. Further, the major interband transitions occur at energies beyond 10 eV in w-ZnS and w-ZnSe, while in w-ZnO they occur also up to 20 eV, in good agreement with the results by Karazhanov et al. [18].

The calculated components of the absorptive part of the dielectric function (Figure 5) exhibit some peaks, labelled E_i ($i = 1, 2, 3, \dots$) while the corresponding peaks in the experimental spectra are labelled e_i ($i = 1, 2, 3, \dots$). It is evident that that some E_i peaks coincide well with the corresponding e_i peaks in the experimental spectra indicated by Adachi et al. [41] (e.g., (e_2 and e_3) at $\epsilon_2^{xx}(w-ZnO)$ and (e_2 and e_4) at $\epsilon_2^{zz}(w-ZnO)$; (e_2 , e_3 and e_4) at $\epsilon_2^{xx}(w-ZnS)$ and e_4 at $\epsilon_2^{zz}(w-ZnS)$, see Tables 2–7. Figure 7 also, depicts the real part of the dielectric function $\epsilon_1(\omega)$ with its two components, $\epsilon_1^{xx}(\omega)$ and $\epsilon_1^{zz}(\omega)$, which traduce the dispersion of the incident electromagnetic radiations with linear optical properties of such medium. As shown in Figure 7, the presented spectra of

the three compounds are distinctively different indicating the relative optical anisotropy in these compounds.

Figure 8a–c shows the components ($n^{xx}(\omega)$ and $n^{zz}(\omega)$) of the calculated refractive index. The estimated static refractive index $n(0)$, the difference $\Delta n(0)$ and the energies for which the dispersion is zero, that is, $E(n = 1)$, are listed in Table 8. From Figures 7a–c and 8a–c, it is noted that, the shapes and energy positions of the main features of the $\epsilon_1(\omega)$ and $n(\omega)$ curves are similar to each other.

The $n(\omega)$ function reaches its maximum value of 3.3 eV (ZnO in xx polarisation), 5.6 eV (ZnS in xx) and 4.99 eV (ZnSe in zz), while the maximum of the $k(\omega)$ function appears at high energy (~ 9.0 eV). Also, one can see with the large band gap estimated, the refractive index of these materials varies from 2.6 to 1.7 in the visible region made them among candidates required for antireflection (AR) coatings.

Additionally, optical anisotropy is an interesting physical property to understand the material response against the electromagnetic excitations. Researchers often exploit

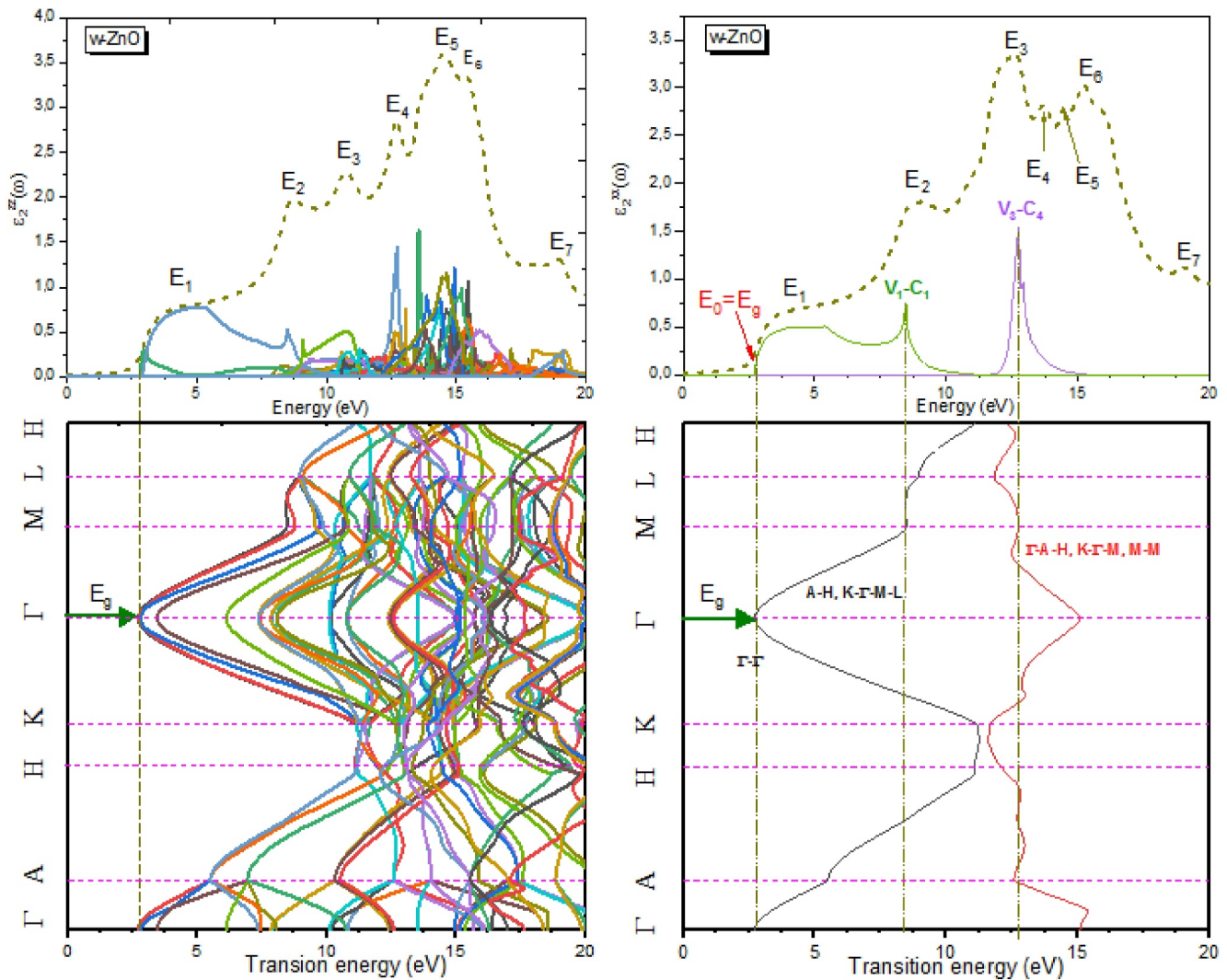


FIGURE 6 Transition energy band dispersion along the band structure path: $E(k) = E_c(k) - E_v(k)$ for ZnO as representative. The (V_1-C_1 and V_3-C_4) inter band transitions arise (E_2 and E_3) structures, respectively. See Ref. [43] and text for details.

anisotropy properties of materials to obtain enhanced performance of devices. The static optical anisotropy for the candidate compounds can be quantified by the anisotropy ratio, which can be expressed as follows [47, 48]:

$$A_{OPT} = \left[\frac{n(0)^{[direction]}}{n(0)^{[average]}}, \frac{\epsilon_1(0)^{[direction]}}{\epsilon_1(0)^{[average]}} \right] \quad (4)$$

Here, $\epsilon_1(0)^{[direction]}$ and $n(0)^{[direction]}$ is the value of $n(0)$ and $\epsilon_1(0)$ along principal optical axes, while $(n(0)^{[average]})$ and $\epsilon_1(0)^{[average]}$ are average values. If $A_{OPT} = 1$, this material is considered optically as isotropic, otherwise, it is optically anisotropic. Each deviation of the A_{OPT} value from unity reveals the extent of the optical anisotropy. According to the zoomed form at zero frequency shown in Figures 7 and 8a–c, one can calculate the theoretical and experimental values of A_{OPT} . The numerical results are listed in Table 8. The

calculated A_{OPT} values reveal that, the studied compounds exhibit a certain optical anisotropy. The maximum experimental optical anisotropy occurs in the ZnO sample along the two principal directions, while the theoretical evaluation exhibit that both ZnS and ZnSe have high A_{OPT} values along (zz) and (xx) directions, respectively. The calculated absorption coefficient $\alpha(\omega)$ is shown in Figure 9. (1–3). This optical parameter quantifies the fraction of energy lost by the incident electromagnetic radiation per unit length of a known medium.

The absorption coefficient $\alpha(\omega)$ reaches its maximum value at approximately: $(2.32 \cdot 10^6 \text{ cm}^{-1}/15.28 \text{ eV})$, $(1.91 \cdot 10^6 \text{ cm}^{-1}/9.46 \text{ eV})$ and $(1.94 \cdot 10^6 \text{ cm}^{-1}/8.53 \text{ eV})$ for w -ZnO, w -ZnS and w -ZnSe, respectively.

Figure 9. (4–6) presents the calculated frequency dependent reflectivity spectra $R(\omega)$. The reflectivity of our compounds increases with increasing photon energy and reaches its maximal value of approximately 37.5%–45% at energies in the range of 8 till 20 eV.

TABLE 2 Peak positions of the $\epsilon_2^{xx}(\omega)$ spectrum together with the dominant inter-band transition contributions to every peak and their location in the whole Brillouin zone of w-ZnO. The peak position and energy are in eV.

Structure		Peak position	Transitions	Contribution parentage	Region transitions	Energy		
E_1	4.82		V_3 - C_2	25.33	A-H, K- Γ -M-L	4.33		
			V_2 - C_3	16.02	A-H, K- Γ -M-L-H	4.58		
			V_1 - C_3	7.02	H-K- Γ	4.63, 4.78		
			V_2 - C_4	12.13	Γ -A-H, K- Γ -M	4.85, 4.94		
			V_2 - C_7	6.52	A-H, K- Γ , M-L	4.68		
$e_2(E_2)$	9.07		V_1 - C_1	18.13	A-H, K- Γ -M-L	8.43		
			V_2 - C_1	22.75	A-H, K- Γ , L-H	8.60		
			V_3 - C_1	17.35	A-H, K- Γ -M-L	9.01		
			V_4 - C_2	11.01	A-H, K- Γ -M-L-H	9.21, 8.09		
			V_2 - C_2	5.06	A-H, K- Γ -M-L-H	9.12		
			V_1 - C_2	17.63	A-H, K- Γ -M, L-L	9.00		
e_3	E_3	12.61	V_{14} - C_1	21.57	A-H, K- Γ -M-L	12.35		
			V_{12} - C_2	2.33	A-H, K- Γ -M-L-H	12.77		
			V_{11} - C_2	4.53	Γ -A-H, Γ - Γ , L-L	12.46, 13.96		
			V_5 - C_3	2.75	Γ -A-H, K- Γ , M-L-H	13.18		
			V_4 - C_3	12.52	Γ -A, K-L, M-M, L-H	12.00, 12.70		
			V_4 - C_4	5.69	Γ -A, K- Γ -M	13.07, 13.15		
			V_3 - C_3	25.62	Γ -A, H-K- Γ , L-H	12.18		
			V_3 - C_4	13.37	Γ -A-H, K- Γ -M, M-M	12.73, 12.94		
			V_2 - C_3	2.56	Γ -A, H-K- Γ -M-L	12.56		
			V_2 - C_4	12.41	A-H, K- Γ -M	11.89, 12.29		
			V_1 - C_4	8.56	Γ -A, K- Γ -M	12.81		
			V_{11} - C_2	35.42	A-H, K-K, K- Γ -M, L-H	13.96		
	E_4	13.70	V_6 - C_3	12.14	Γ -A-H, K- Γ , L-H	13.59		
			V_6 - C_4	5.87	A-H, K- Γ -M-L	13.90		
			V_5 - C_4	5.45	A-H, K- Γ -M, L-H	13.57		
			V_2 - C_5	5.11	A-H-K- Γ -M-L-H	13.87, 14.44, 15.20		
			V_1 - C_5	5.63	A-H-K- Γ -M-L-H	13.84		
			E_5	14.52	V_2 - C_5	38.56	A-H, K-K, K- Γ -M-L-H	14.44
					V_4 - C_5	15.66	A-H-K, L-H	14.41, 15.05
					V_3 - C_5	3.49	A-H-K, M-L-H	14.45, 14.91
	V_1 - C_6	12.15			A-H, K- Γ , L-H	14.59, 15.16		
	E_6	15.22	V_4 - C_5	5.45	A-H-K- Γ -M	15.05		
			V_3 - C_5	2.83	A-H, K- Γ -M	14.91		
			V_1 - C_6	7.64	Γ -A-H, K- Γ -M-L	15.16		
			V_{14} - C_4	19.5	A-H, K- Γ -M-L	15.70		
			V_{13} - C_4	12.25	A-H, K- Γ -M	15.56		
			V_{12} - C_4	6.53	A-H, K- Γ -M-L	15.22		

TABLE 2 (Continued)

Structure	Peak position	Transitions	Contribution parentage	Region transitions	Energy
E_7	19.03	$V_{11}-C_4$	5.89	A-H, K-I-M, L-H	15.17, 15.32
		V_5-C_5	5.22	A-H-K-I, L-H	15.34
		V_3-C_6	3.15	I-A-H, K-I, M-H	15.57
		V_2-C_6	5.75	I-A-H, K-I-M-L-H	15.11
		V_2-C_7	5.35	I-A-H, K-I-M	16.01
		V_1-C_7	2.16	A-A, K-I	15.45
		$V_{16}-C_5$	18.28	A-H, K-I-M, L-L	18.94
		$V_{14}-C_6$	26.36	A-H, K-I-M-L	19.42
		V_2-C_9	5.48	A-H, K-I, L-H	19.36
		V_1-C_9	8.30	A-H, K-I, M-L	19.14
		V_4-C_8	12.15	A-H-K, L-H	18.72

The optical photoconductivity $\sigma(\omega)$ spectra are depicted in panels (a–g) in Figure 10. The real part ($\sigma_1(\omega)$) of the conductivity function is negligible for photon energy in the band gap. Beyond the forbidden band (E_g), this physical quantity arises rapidly in the UV spectral range confirming that these compounds are of great importance in the visible-to-ultra-violet sensing, for photo-conducting cells, in luminescent devices and solar energy harvesting.

3 | EXPERIMENTAL SETUP

3.1 | Samples preparation

Via the ultrasonic pyrolysis method and ambient conditions, our ZnO thin films were grown on silicon substrates inside a fume cupboard. The precursor solution of 0.4 M concentration was prepared by dissolving ($ZnC_4H_6O_4 \cdot 2(H_2O)$) zinc acetate dehydrate (Sigma Aldrich, 4N: 99.99% purity) in 0.1 L of methanol. The obtained solutions were stirred over 60 min in order to achieve a homogeneous solution. The spray growth was made using a flux of air over the heated Si substrates (450°C).

The ZnS thin films were deposited on glass substrates with dimensions of $10 \times 5 \times 2 \text{ mm}^3$ made of soda-lime glass. The thermal evaporator (BALZERS BA 510 Vacuum Evaporator) was used in the growth process, in which the closed preparation chamber possesses a residual pressure of about 5×10^{-6} mbar. The thermal evaporation was realised by massif pieces of solid ZnS (BIOCHEM Chemo pharma, $\geq 98\%$ high purity). We used also a commercial piece of w -ZnSe (110-1) with dimensions of about $7 \times 5 \times 1.7 \text{ mm}^3$ purchased from Neyco, a company for vacuum and materials, and it appears orange to the naked eye. All the samples were subjected to an ultrasonic bath as an ex situ chemical treatment, which is explained in the next paragraph.

3.2 | Ultra high VACUUM conditions

The vacuum level is an extremely important physical parameter in the engineering of thin films from the points of view of synthesis processes and sample characterisations.

Any systematic variation in VL affects relative features of the elaborated samples and also the reliability of the results achieved. The ultra-high purity environment leads us to carry out high precision spectroscopic investigations based on (electrons, photons, ions)–matter interactions [27]. Therefore, the environment purity level must be taken into consideration in samples storage, in “in situ” cleaning and becomes a decisive factor in characterisations [49]. Our equipment reaches a final vacuum stage up to (5 to 2.3). 10^{-10} mbar via three principal pumping stages (primary one using RV5 EDWARDS rotary pump, secondary one using HiPace 300 PFEIFFER pump and finally with TSP: titanium sublimation pump from gamma vacuum TSP up to 2.3 10^{-10} mbar). Therefore, achievement of high pure analysis environment is the principal goal of recent works. Schroeder et al. [50] show the necessity of the ultra-high vacuum for industry-relevant thin film growth via magnetron sputtering and cathodic arc deposition. Dorri et al. [51] show a high structural quality hetero epitaxial $CrB_x(0001)/TiB_y(0001)$ synthesised under UHV condition. Shin et al. [52] explore successfully the possibility of obtaining stoichiometric epitaxial δ -TaN thin films, high-quality and dense by ultrahigh vacuum reactive magnetron sputtering.

3.3 | Sample treatments

3.3.1 | Ultrasonic bath (ex-situ cleaning)

The samples were cleaned ex situ with an ultrasonic bath ($f = 40 \text{ KHz}$) against the ubiquitous impurities in laboratory (i.e., O, -(OH) groups, H and CO_x species), with acetone

TABLE 3 Peak positions of the $\epsilon_2^{zz}(\omega)$ spectrum together with the dominant inter-band transition contributions to every peak and their location in the whole Brillouin zone of w-ZnO. Peak position and energy are in eV.

Structure	Peak position	Transitions	Contribution percentage	Region transitions	Energy
E_1	4.87	V_3-C_3	55.16	A-H, K- Γ -M-L	4.12
		V_1-C_3	16.42	A-H, K- Γ -M-L-H	4.55
		V_3-C_5	5.33	H-K- Γ	4.63
		V_2-C_4	12.43	Γ -A-H, K- Γ -M	4.81
		V_2-C_6	2.75	A-H, K- Γ , M-L	4.34, 4.65
$e_2(E_2)$	8.72	$V_{14}-C_1$	5.16	Γ -A, K- Γ -M	8.31
		$V_{13}-C_1$	5.85	Γ -A, K- Γ -M	8.96
		V_4-C_2	28.30	A-H, K- Γ -M	8.87
		V_3-C_1	36.04	A-H, K- Γ -M	7.89
		V_2-C_1	15.57	A-H, K- Γ -M-L	8.52
		V_2-C_2	12.48	A-H, K- Γ -M, L-H	9.09
		V_1-C_1	30.16	A-H, K- Γ -M-L	8.50
$e_3(E_3)$	10.76	$V_{14}-C_1$	4.18	A-H, K- Γ -M	11.22
		V_1-C_3	5.23	Γ -A, H-K- Γ , M-L-H	10.83, 11.28
		$V_{13}-C_1$	5.48	Γ -A, K- Γ -M	10.02
		V_5-C_1	13.62	A-H, K- Γ -M	10.57
		V_5-C_2	11.02	A-H, K- Γ -M, L-L	10.94
		V_2-C_3	5.07	Γ -A, K- Γ -M	10.65, 11.40
		V_3-C_2	17.16	A-H-K- Γ -M, L-H	11.36
		V_2-C_2	10.75	A-H, K- Γ , L-H	10.74
		$V_{16}-C_1$	43.66	H-H, L-H	13.00
e_4	E_4	V_2-C_4	12.41	A-H, K- Γ -M	12.30
		V_3-C_4	11.15	Γ -A, K- Γ -M	12.64, 13.06
		V_5-C_2	7.88	A-H-K- Γ -M, L-H	12.76
		V_6-C_3	5.06	Γ -A-H, K- Γ -M-L-H	13.54
		V_5-C_3	12.43	Γ -A, K- Γ -M	12.60
		V_5-C_4	21.77	A-H, K- Γ , L-H	13.40
		V_4-C_3	6.03	A-H-K- Γ	12.75
		V_4-C_4	5.82	A-H-K, Γ -M-L	12.80, 13.08
		V_1-C_5	7.12	A-H-K- Γ -M-L-H	13.84
	E_5	$V_{16}-C_2$	6.02	H-K- Γ -M, L-H	14.94
		$V_{15}-C_2$	12.15	A-H-K- Γ -M, L-H	14.74
		$V_{13}-C_2$	6.02	A-H-K- Γ , L-H	14.39
		V_2-C_5	2.33	A-H-K- Γ -M-L-H	13.87, 14.38
		V_7-C_4	5.48	A-H, K- Γ -M-L	14.10
		V_4-C_5	12.35	A-H-K, M-L, L-L	14.63
		V_3-C_6	18.56	A-H, K- Γ , L-H	14.79
		V_1-C_6	11.02	A-H, K- Γ , M-L-H	14.65
	E_6	V_5-C_5	17.25	A-H-K- Γ , L-H	15.33, 15.50, 15.57
		$V_{16}-C_3$	5.89	H-K, M-M	15.01, 15.55

TABLE 3 (Continued)

Structure	Peak position	Transitions	Contribution percentage	Region transitions	Energy
E_7	18.95	V_4-C_7	4.74	$\Gamma-A-H, K-\Gamma$	16.56
		$V_{13}-C_4$	5.27	$A-H, K-\Gamma-M-L-H$	15.46
		$V_{11}-C_3$	10.76	$A-H, K-\Gamma, \Gamma-\Gamma, L-H$	15.10
		$V_{11}-C_4$	3.55	$A-H, K-\Gamma-M-L$	15.14, 15.32
		V_3-C_6	12.15	$\Gamma-A, K-\Gamma-M-L$	15.74
		V_6-C_5	6.85	$A-H-K, \Gamma-M-L-H$	15.78
		V_1-C_7	5.49	$\Gamma-A-H, K-\Gamma-M$	15.95
		V_2-C_6	12.12	$\Gamma-A-H, K-\Gamma-M-L$	15.21
		V_2-C_7	10.73	$\Gamma-A-H, K-\Gamma$	15.91, 16.24
		V_1-C_8	3.22	$A-H, K-\Gamma-M$	16.71
		$V_{16}-C_5$	12.25	$A-H, K-\Gamma-M-L-H$	18.27, 19.36
		$V_{10}-C_7$	16.18	$\Gamma-A-H-K-\Gamma-M, L-H$	19.41
		V_4-C_8	2.33	$A-H-K, L-H$	18.72
		V_9-C_7	3.28	$A-A, H-K-\Gamma-M-L$	18.92
		V_2-C_9	5.66	$A-H, K-\Gamma-M-L$	18.12, 19.22
		V_1-C_9	2.43	$A-H, K-\Gamma, L-H$	19.14
		V_8-C_7	6.82	$\Gamma-A-H-K-\Gamma-M-L$	19.10
		V_7-C_7	5.93	$A-A, H-K-\Gamma-M-L$	18.84

Note: The bold values in theoretical section (VIZ. Gathered in tables are in well coincidence with the experimental ones that collected from UHV REELS technique).

solution (5 min), ethanol (5 min) and in deionised water at room temperature (RT) (5 min). Next, the samples were dried by highly purified nitrogen gas (N_2) flow of 6N (99.9999%) and prepared to the mechanical introduce at our analysis apparatus.

3.3.2 | Ultra high vacuum treatment (in-situ cleaning)

We introduced the samples carefully onto a rotating sample holder at a FEL chamber (Fast Entry Lock), which belongs to the UHV analysis system, designed and produced by Scienta Omicron Surface Nano Analysis GmbH Company, Uppsala, Sweden Figure 11.1. As aforementioned, a close monitoring of VL evolution in the whole instrumentation must be taken in consideration during the annealing process, ionic bombardment, outgas of the filament, degas of the anodes and so on. The first operation is the Ar^+ ions sputtering, carried out by the ion gun of cold cathode-sputter ion source ISE5-in the preparation chamber Figure 11.2. Using the leak valve, the Argon gas introduction was fixed at 0.8 Langmuir (1Langmuir corresponds to 10^{-6} Torr/s). The vacuum now is of 5.7×10^{-6} mbar, readable at a Penning gauge. The current density, the energy and total Ar^+ flux are

about 12 mA/cm², 1.2 keV and $4.2 \cdot 10^{16}$ ions/cm², respectively, for 40 min.

In a second step, we heated the sample with a rate of 40°C/min up to 350°C (during 20 min) with a rate of 50°C/min up to 500°C(during 20 min) and with a rate of 50°C/min up to 650°C(during 40 min) ensured by a digital sample holder. The sample temperature was measured by a PBN (Pyrolytic Boron Nitride) thermocouple. During this heating process the VL change clearly and distinctly as shown in Figure 11.3. Then, the system was progressively cooled down to RT for about 1h. At last, we introduce a titanium sublimation over 1 min to reach a vacuum better than $<5 \cdot 10^{-10}$ mbar measured using Bayard–Alpert ion gauges. We reanalysed samples after with the same techniques.

3.4 | Characterisation section

In the X-PES analysis, the samples were irradiated by a DAR400 monoenergetic X-rays source with Al/Mg anodes that allow Al $K\alpha$ (1253.6 eV)/Mg $K\alpha$ (1486.6 eV) radiations to be selected. A continuous vigilance must be taken during this analysis, in which the base VL must be greater than $5 \cdot 10^{-8}$ mbar. The (photons, electrons)-matter interaction spot area was about 1 mm², any variation of the target size,

TABLE 4 Peak positions of the $\epsilon_2^{xx}(\omega)$ spectrum together with the dominant inter-band transition contributions to every peak and their location in the whole Brillouin zone of w-ZnS. Peak position and energy are in eV.

Structure	Peak position	Transitions	Contribution percentage	Region transitions	Energy
E_1	6.49	V_5-C_2	6.18	Γ -A, K- Γ -M	5.30, 5.42
		V_3-C_1	9.42	Γ -A, K- Γ -M-L-H	6.38
		V_2-C_1	23.25	A-H, K- Γ , L-H	6.44
		V_2-C_2	46.23	A-H, K- Γ -M-L-H	6.42
		V_1-C_1	52.18	A-H, K- Γ , M-L	5.70, 6.11
		V_1-C_2	9.17	A-H, K- Γ -M, L-H	6.06, 6.27, 6.51
		V_4-C_2	12.14	A-H, K- Γ -M-L-H	6.46
$e_2(E_2)$	6.84	V_3-C_2	6.92	A-H, K- Γ -M-L-H	6.85
		V_4-C_1	5.43	A-H, K- Γ -M-L-H	7.10
		V_3-C_1	8.34	A-H, K- Γ , L-H	6.83
		V_3-C_2	7.11	A-H, K- Γ -M-L-H	6.85, 6.93
		V_2-C_1	32.23	A-H, H-H, K- Γ	6.87
		V_2-C_2	27.17	A-H, K- Γ , M-M, L-H	6.91
$e_4(E_3)$	7.74	V_5-C_3	8.25	Γ -A, Γ - Γ	8.02
		V_4-C_3	9.14	Γ -A-H, K- Γ -M-L-H	7.89, 7.74
		V_3-C_3	7.31	Γ -A-H, K- Γ -M-L-H	7.72
		V_2-C_3	8.19	Γ -A-H, K- Γ -M-L	7.48b
		V_2-C_4	2.13	Γ -A-H, K- Γ -M-L-H	7.82
		V_1-C_3	63.04	Γ -A-H, K- Γ , M-L	7.37, 7.50
		V_1-C_4	16.22	Γ -A-H, K- Γ -M-L-H	7.78
$e_5(E_4)$	9.10	V_6-C_1	8.11	Γ -A-H, Γ - Γ	8.72
		V_6-C_2	5.23	A-H, K- Γ -M, L-H	9.51, 9.74, 9.93
		V_3-C_6	3.93	A-H, K- Γ -M	8.79
		V_1-C_7	2.19	A-H, Γ - Γ	8.44
		V_2-C_5	3.52	K- Γ -M-L-H	9.60
		V_1-C_5	15.17	A-H, K- Γ -M-L	8.98
E_5	10.79	$V_{15}-C_2$	2.09	A-H, K- Γ -M, L-H	11.36
		$V_{13}-C_2$	2.34	A-H, K- Γ -M	11.21
		$V_{12}-C_1$	5.14	A-H, K- Γ -M, L-H	10.91
		$V_{12}-C_2$	6.78	A-H, H-H, K- Γ -M, L-H	11.18
		V_6-C_1	31.19	K- Γ -M, L-H	9.86
		V_2-C_6	6.64	H-K- Γ , M-M, M-L-H	10.40, 10.53, 10.62
		V_6-C_3	16.16	Γ -A-H-K- Γ -M-L-H	10.70

less or more than could be the reason of a structural deterioration or signal dispersion, respectively. The UHV-REELS technique was carried out with a high-performance electron gun, using a hexa-boride lanthanum LaB₆ filament “SL 1000 SPA”. The records were in direct mode with three primary ($E_p = 900, 700$ and 500 eV) exciting energies. The PLS optical technique was performed

with high quality equipment, which contained a spectrometer HORIBA iHR-550 equipped with a charge-coupled device CCD image sensor (400–1000 nm) and an InGaAs detector (800–1600 nm). Also, a He-Cd gas laser ($\lambda = 325$ nm and $P = 30$ mWatt) was used as the excitation source. Besides, in the UV-vis analysis, the photonic absorbance of ZnCh thin films was examined by a Shimadzu UV-3101

TABLE 5 Peak positions of the $\epsilon_2^{zz}(\omega)$ spectrum together with the dominant inter-band transition contributions to every peak and their location in the whole Brillouin zone of w-ZnS. Peak position and energy is in eV.

Structure	Peak position	Transitions	Contribution percentage	Region transitions	Energy
$e_2(E_1)$	6.52	V_3-C_1	12.18	A-H, K- Γ , L-H	6.91
		V_2-C_1	16.28	A-H, K- Γ -M-L	5.81
		V_2-C_2	25.66	A-H, K- Γ -M-L-H	6.34, 6.91
		V_1-C_1	5.23	A-H, K- Γ , L-H	6.56, 6.80
		V_1-C_2	58.22	A-H-K- Γ	6.99
E_2	7.66	V_4-C_2	12.18	A-H, K- Γ -M-L-H	7.47
		V_3-C_1	24.23	A-H, K-K, K- Γ , L-H	7.28
		V_3-C_3	16.16	Γ -A, K- Γ -M, L-L	7.66
		V_3-C_2	5.93	A-H, K- Γ , L-H	7.99
		V_2-C_1	7.43	A-H-K- Γ	7.13
		V_2-C_3	5.11	Γ - Γ , K- Γ -M	7.22
		V_2-C_4	3.22	Γ -M, Γ - Γ , Γ -A	7.82, 8.23
		V_1-C_3	3.01	Γ -A-H, K- Γ , M-L	7.52
		V_1-C_4	5.44	Γ -A-H, K- Γ -M-L-H	7.78
		V_6-C_1	6.18	Γ -A-H	8.73
$e_3(E_3)$	8.45	V_6-C_2	8.91	A-H, K- Γ -M-L-H	9.51
		V_5-C_1	8.77	A-H-K, M-L	8.67, 9.11
		V_4-C_3	5.02	A-H, K- Γ -M-L-H	8.34, 9.12
		V_4-C_4	3.44	A-H, K- Γ -M-L-H	8.49
		V_3-C_4	2.45	A-H, K- Γ -M-L	8.31
		V_1-C_5	2.21	A-H, K- Γ -M	8.38, 8.84
		$V_{16}-C_1$	7.96	A-H, K- Γ -M-L-H	10.75
E_4	10.49	$V_{15}-C_1$	3.51	Γ -A-H, K-K, K- Γ -M, L-H	11.03
		V_6-C_2	3.88	A-H, K- Γ -M-L-H	9.74, 9.93
		V_3-C_8	13.27	Γ -A-H, K- Γ -M	10.19
		V_4-C_5	5.38	A-H, K- Γ -M-L-H	10.76
		V_4-C_6	2.85	A-H, K- Γ -M, L-H	10.79
		V_3-C_5	17.82	A-H, K- Γ -M-L	10.38, 9.94
		V_1-C_{10}	2.60	Γ -A, K- Γ -M	10.46
		$V_{16}-C_3$	6.97	A-H-K- Γ -M-L-H	12.54
		$V_{15}-C_2$	7.36	H-K- Γ	11.97
		$V_{15}-C_3$	10.22	H-K, Γ -M-L-H	12.30
$e_4(E_5)$	12.34	$V_{14}-C_3$	9.56	H-K- Γ -M, L-H	12.46
		$V_{11}-C_4$	3.44	Γ -A-H-K- Γ -M-L	12.89
		$V_{10}-C_3$	3.17	A-H-K- Γ -M, L-H	12.27
		V_6-C_5	5.52	A-H, K- Γ -M, L-H	12.52
		V_5-C_6	3.04	H-K, Γ -M, L-H	12.63
		V_5-C_7	2.13	A-H, K- Γ -M	12.50
		V_3-C_7	4.78	A-H, K- Γ -M-L-H	11.99
		V_1-C_9	6.20	Γ -A, K- Γ -M	12.32

(Continues)

TABLE 5 (Continued)

Structure	Peak position	Transitions	Contribution percentage	Region transitions	Energy
E_6	13.62	$V_{16}-C_4$	6.74	A-H, K- Γ , Γ - Γ , M-L-H	13.09
		$V_{16}-C_5$	2.45	A-H, K- Γ -M	13.78
		$V_{15}-C_4$	5.13	Γ -A-H-K- Γ -M-L	13.11, 13.36, 13.51
		$V_{14}-C_4$	2.02	A-H, K- Γ , M-L-H	13.01
		$V_{14}-C_5$	1.98	A-H, K- Γ -M-L	13.82, 14.01
		$V_{13}-C_4$	5.33	H-K- Γ	13.04
		V_6-C_6	2.28	Γ -A, K- Γ -M, L-H	13.13
		V_3-C_{11}	3.16	A-H, K- Γ -M	13.65
E_7	18.87	$V_{14}-C_{11}$	5.23	A-H-K- Γ -M	18.95, 19.08
		$V_{13}-C_{12}$	5.81	Γ -A-H-K- Γ -M	18.80, 19.27
		$V_{12}-C_{11}$	5.16	A-H-K- Γ -M	18.84
		V_8-C_{11}	5.42	A-H-K- Γ -M	18.38
		V_8-C_{12}	5.37	A-H-K- Γ -M-L-H	18.91
		V_6-C_{12}	5.19	A-H-K- Γ -M	18.00
		V_6-C_{11}	2.82	A-H-K, M-M	18.08

PC-spectrophotometer for solids under atmospheric environment and UVvis excitation source.

4 | RESULTS AND DISCUSSION

4.1 | Chemical composition study

4.1.1 | X-PES results (ex-situ cleaned and after controlled UHV treatment)

Noteworthy, the spectroscopy [27] and imagery [49] are two important scientific trends, essential to understand the physicochemical properties of thin-layer materials. They are performed as combinatorial in situ techniques for materials properties study with high precise results. For example: imaging techniques such as (scanning) transmission electron microscopy/energy dispersive X-Ray ((S) TEM/EDX) allow experimentalists to visualise the upper layer morphology and their cross sectional images. According to the latter, the size and shape of particles at the atomic scale are identified. Recently, the (S) TEM/EDX techniques demonstrated that many physical factors do induce significant changes in the ground state features of thin films. Ayon et al. [53] report using field emission scanning electron microscopy and transmission electron microscopy (FESEM and TEM) images, a reduction in particle size and considerable change in topography of Sm^{3+} doped ZnO. Shao et al. [54] found that TEM imagery technique is very helpful to construct a hetero junction of ZnS/ Sb_2S_3 designed for high performance sodium storage. Qiu et al. [55] report the importance of including UHV (High Resolutions TEM, TEM)/SEM images for characterising a highly twinned ZnSe nano-rods prepared to enhance the

electrochemical gas conversion $\text{N}_2(\text{gas}) \rightarrow \text{NH}_3(\text{gas})$. Therefore, in our case we aim to show the correspondence between UHV-(XPES, REELS and PLS) techniques and zero pressure-DFT computer calculations as closely as possible.

The X-PES source was equipped with a controlled cooling system that keeps the X-ray source under a constant internal temperature of about 20°C. The analysis depth with X-PES technique is about 10 Å. During the X-PES spectra records, we used a constant pass energy equal to 30 eV and CAE = 50. The initial state (ex situ cleaning) of the sample surfaces was examined in detail in the analysis chamber of the UHV system. We fully clarify on the basis of X-PES, AES, REELS, UPS, PLS and AFM techniques [5, 56] that the contaminant species (e.g., the presence of O, H, CO_x and -(OH) groups at the sample surface) of thin layers can be identified. During annealing process, one could observe a distinct change in VL Figure 11. 3, indicating that our vacuum instrumentation was very sensitive to the residual gases contamination which is attributed to the H, hydroxyl groups and CO_x desorption phenomenon. The sample heating under UHV leads to facilitate a complete thermodynamic O segregation. For example, in thin films of w-ZnO, we show a whole change in crystallisation due to the surface elemental modification shown in Figure 12 (Checked by X-PES and AFM images) [56].

Furthermore, a total disappearance of the optical response (green luminescence 540 nm (2.3eV) attributed to total O bulk segregation and other red emission of $H_i \rightarrow V_O$ transition 775 nm (1.6eV)) occurs as a result of H desorption phenomena, which contribute in fact to a relative change in the optical and structural properties of our thin layers (checked by Photo-Luminescence Spectroscopy and Atomic Force Microscopy) [56]. The main peak positions (see Figure 13) are in good agreement with other experimental measurements of the related

TABLE 6 Peak positions of the $\epsilon_2^{xx}(\omega)$ spectrum together with the dominant inter-band transition contributions to every peak and their location in the whole Brillouin zone of w-ZnSe. Peak position and energy are in eV.

Structure	Peak position (eV)	Transitions	Contribution percentage	Region transitions	Energy (eV)
E_1	5.67	V_4-C_2	2.69	A-H, K- Γ -M	5.07
		V_3-C_1	35.85	A-H, K- Γ -M-L-H	5.58
		V_2-C_1	52.03	A-H, K- Γ , L-H	5.65
		V_2-C_2	12.91	A-H, K- Γ -M-L-H	5.73
		V_1-C_1	57.16	A-H, K- Γ , M-L	5.36, 5.97
		V_1-C_2	12.75	A-H, K- Γ -M-L	5.27
E_2	6.08	V_4-C_1	8.30	A-H, K- Γ -M-L-H	6.68
		V_3-C_2	12.26	A-H, K- Γ -M-L-H	6.11, 6.25
		V_2-C_3	7.12	Γ -A-H, K- Γ -M-L-H	6.95
		V_1-C_3	3.15	Γ -A-H, K- Γ , M-L	6.84
		V_3-C_1	8.56	A-H, K- Γ -M, M-M, L-H	6.07
		V_1-C_3	10.58	Γ -A, K- Γ -M-L	6.73, 6.84
		V_4-C_2	5.36	A-H, K- Γ -M-L-H	6.80
		V_1-C_1	17.25	H-K- Γ	6.56
E_3	7.12	V_3-C_3	8.07	Γ -A-H, K- Γ -M	7.08
		V_3-C_5	10.55	Γ -A, K- Γ -M-L-H	7.63
		V_4-C_3	13.24	Γ -A-H, K- Γ -M	7.32
		V_2-C_4	2.66	Γ -A-H, K- Γ -M-L-H	7.20
		V_2-C_6	2.12	Γ -A-H	7.72
		V_1-C_3	7.86	A-A, A-H-K- Γ , L-H	7.75
		V_1-C_6	2.13	Γ -A-H, K- Γ -M	7.73, 7.51
		V_1-C_4	2.46	Γ -A-H, K- Γ -M-L-H	7.82
E_4	8.53	V_6-C_1	5.31	A-H, K- Γ	8.44
		V_6-C_2	6.02	A-H, K- Γ -M-L-H	8.82
		V_5-C_4	5.81	A-H, K- Γ -M	8.70, 9.07
		V_3-C_6	10.71	Γ -A-H, K- Γ -M	8.25
		V_2-C_5	2.18	A-H, K- Γ -M	8.52
		V_2-C_7	2.73	A-H, K- Γ -M	8.72
		V_1-C_5	5.23	A-H, K- Γ -M-L	8.35
E_5	10.11	$V_{14}-C_1$	3.04	A-H, K- Γ -M, L-H	10.53
		V_6-C_3	2.87	Γ -A-H-K- Γ -M-L-H	10.41
		V_6-C_4	2.14	Γ -A-H, K- Γ , M-L-H	10.87
		V_2-C_{10}	3.86	Γ -A, Γ -M	10.15
		V_4-C_6	5.44	K- Γ -M	10.70, 10.52
		V_4-C_7	5.13	A-H, K- Γ -M	10.16
		V_4-C_5	2.29	A-H, K- Γ -M-L-H	10.19
E_6	13.45	V_1-C_{10}	5.25	A-A, A-H-K- Γ -M, L-H	13.25
		V_1-C_{11}	3.16	A-H, K- Γ -M	13.16, 13.37
		V_1-C_{12}	5.73	A-H-K- Γ -M	13.47
		$V_{16}-C_6$	5.71	Γ -A-H, L-H	13.89, 13.93

(Continues)

TABLE 6 (Continued)

Structure	Peak position (eV)	Transitions	Contribution percentage	Region transitions	Energy (eV)
		V ₁₄ -C ₆	5.12	Γ-A-H, K-Γ, L-H	13.81
		V ₁₄ -C ₅	5.03	A-H, K-Γ-M-L	13.54, 13.62

Note: The bold values in theoretical section (VIZ. Gathered in tables are in well coincidence with the experimental ones that collected from UHV REELS technique).

compounds. All features of the survey X-PES spectra depicted in Figures 13 and 14b,b measured for as tested ZnCh crystal surfaces are fairly attributed to the core levels and Auger lines of the atoms constituting the binary chalcogenide [57–59]. There is no indication of any other chemical elements except faint signals and barely visible of (C and O) 1s Figure 14b,c. According to the X-PES spectra presented in Figure 13, the relative intensities change as a result of such in situ cleaning. Particularly, Ar⁺ ionic bombardment of thin film surface causes significant modification in the topmost layer of thin films. Regarding the peak area of the C 1s core-level spectrum (before in Figure 14c and after in Figure 14d treatment), a pronounced decrease in the relative intensity of the C1s peak by about −93.75% in ZnO, −87.33% in ZnS and −82.27% in ZnSe is detected. On the other hand, the main spectral features associated with zinc (Auger Zn L₃M₄₅M₄₅ line, X-PES core-level Zn 2p_{1/2}, Zn 2p_{3/2}, and Zn 3d spectra) increase their relative intensities by about +5% to +10% as illustrated in Figure 15a–c. These changes in the core-level and Auger spectral peak features are attributed to the elimination of the suppressing effect due to the contaminants after the controlled treatment. Furthermore, a comparative observation of the Zn 3d core-level spectra of the titled compounds, enable us to see that: the experimental records presented in are in good conformity with the pseudo DOS curves illustrated previously (see Figure 4) in the theoretical part. The observed change in Zn 3d electronic contribution (w-ZnO → w-ZnS → w-ZnSe) indicates that the peak area, full width at half maximum (FWHM) value, peak location and normalised intensity are affected by the change on the electronic competition of the adjacent chalcogenide atoms in such compound. We are also interested in probing the stoichiometry and the homogeneity of the prepared samples. To probe these important features, the modified auger parameter was estimated using the following formula:

$$\alpha' = E_{\text{Kinetic}}(\text{Zn } L_3M_{45}M_{45}) + E_{\text{Binding}}(\text{Zn } 2p_{3/2}) \quad (5)$$

Where: E_{Kinetic} , E_{Binding} are the kinetic, binding energies of Zn L₃M₄₅M₄₅ Auger line and the photoelectron Zn 2p_{3/2}, respectively, measured in (eV). Thus, the estimated modified auger parameters are: (2010.6 ± 0.1) eV, (2011.2 ± 0.2) eV and (2011.8 ± 0.1) eV for w-ZnO, w-ZnS, and w-ZnSe, respectively, in good concordance with other works [5, 60, 61], which confirm the crystallisation of homogeneous hexagonal structures w-ZnCh after an efficient UHV physical treatment.

4.1.2 | The valence orbital features as evidenced from REELS spectroscopy and EELF function

It is of great importance to understand vibrational features and electronic states in the upper surface layers of materials designed for ultra-sensing applications. Studies of the dynamics of propagating and localisation of surface and volume plasmons are very important in this regard. In this work, we adopt REELS (reflective electron energy loss spectroscopy) features in AES (auger electron spectroscopy) at low voltages of losses (i.e. low energies of losses) which involve surface and bulk plasmons and interband transitions. Therefore, REELS spectroscopy is a fundamental and extremely powerful experimental technique for such investigations.

The calculated electron energy loss function (EELF) spectra as main optical parameter can be derived from the components $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ of the dielectric function as follows [37]:

$$L(\omega) = \frac{\epsilon_2(\omega)}{\epsilon_1(\omega)^2 + \epsilon_2(\omega)^2} \quad (6)$$

Experimental setups are often made to verify theoretical predictions. We present in Figure 16 measurements of the distribution of valence electrons associated with atoms constituting ZnCh (Ch = O, S and Se) compounds via experimental REELS and the predictive EELF data. It is worth mentioning that during REELS measurements the residual pressure in an analysing chamber should be better than 5×10^{-8} mbar. In the present REELS experiments we used an SL 1000 electron gun supplied with a LaB₆ filament which allows gaining current density of $38 \text{ A} \cdot \text{cm}^{-2}$ with spot area of 1 mm^2 . The whole electron gun is covered by an efficient μ -metal to keep out any external electromagnetic field perturbations. The REELS spectra were recorded in the direct mode with energy resolution of 0.2 eV for just three primary excitation energies ($E_p = 500 \text{ eV}$, $E_p = 700 \text{ eV}$ and $E_p = 900 \text{ eV}$). The collected electrons are analysed by an Argus electron spectrometer with the constant retard ratio mode (CRR) equal to 50. In this contribution we present REELS and EELF spectra together and adjusted on a common energy scale. Therefore, for the two principal light polarisations (xx) and (zz), the DFT calculations of the L^{xx} and L^{zz} curves show good coincidence and relative compatibility of the fine-structure peculiarities compared with experimental REELS spectra. The L^{xx} and L^{zz} predictive spectra appear different which

TABLE 7 Peak positions of the $\epsilon_2^{zz}(\omega)$ spectrum together with the dominant inter-band transition contributions to every peak and their location in the whole Brillouin zone of w-ZnSe. Peak position and energy are in eV.

Structure	Peak position	Transitions	Contribution percentage	Region transitions	Energy
E_1	5.70	V_3 - C_1	42.15	A-H, K- Γ -M-L-H	5.82
		V_2 - C_1	56.02	A-H, K- Γ -M	5.07
		V_2 - C_2	12.13	A-H, K- Γ -M-L-H	5.60
		V_1 - C_1	38.15	A-H, H-H, K- Γ , L-H	5.97
E_2	7.01	V_3 - C_3	10.12	Γ -A, K- Γ -M-L-H	7.10
		V_3 - C_2	8.25	A-H, K- Γ , L-H	7.43
		V_3 - C_5	3.31	Γ -A, K- Γ -M	7.37
		V_2 - C_3	3.18	A-H-K- Γ , L-H	6.95
		V_2 - C_4	6.24	Γ -A-H-K- Γ , M-L-H	7.19
		V_1 - C_3	63.45	A-A, A-H-K- Γ , L-H	7.25
		V_1 - C_4	14.78	Γ -A-H, K- Γ -M-L-H	7.64, 7.51, 7.85
E_3	7.82	V_5 - C_5	10.28	Γ -A, K- Γ -M	7.93
		V_4 - C_3	9.01	Γ -A, K- Γ -M-L-H	7.72
		V_3 - C_4	12.64	Γ -A, K- Γ -M-L	7.71
		V_4 - C_4	3.30	Γ -A, K- Γ -M-L-H	7.87
		V_2 - C_4	5.26	Γ -A, Γ -M-L-H	7.67
		V_1 - C_5	17.15	A-H, K- Γ -M	7.68
		E_4	9.76	V_6 - C_2	12.46
V_6 - C_4	6.12			A-H	9.18
V_6 - C_1	5.94			H-K- Γ	9.39
V_5 - C_3	5.11			Γ -A-H, K- Γ -M	9.35
V_3 - C_8	3.02			Γ -A-H, Γ -M	9.72
V_2 - C_5	3.22			K- Γ -M-L-H	9.02
V_2 - C_6	3.94			H-K- Γ , M-L-H	9.99
V_2 - C_8	3.13			Γ -A-H, K- Γ , Γ - Γ	9.76
E_5	11.96	V_{10} - C_3	2.49	A-H-K- Γ -M, L-H	11.97
		V_6 - C_5	8.17	A-H, K- Γ -M	11.80
		V_{15} - C_2	2.01	H-K- Γ	11.69
		V_5 - C_8	2.55	A-H, K- Γ -M	11.95
		V_5 - C_9	2.39	Γ -A, K- Γ -M	11.70
		V_{15} - C_3	2.17	H-K, Γ -M-L-H	11.93, 12.23
		V_3 - C_7	3.08	A-H, K- Γ -M-L-H	11.46
E_6	13.51	V_{14} - C_5	6.22	A-H, K- Γ -M-L	13.56
		V_{10} - C_5	5.16	A-H, K- Γ -M	13.03, 13.18
		V_9 - C_5	3.89	A-H, K- Γ -M-L	13.29
		V_9 - C_6	2.11	A-H, L-H	13.51
		V_6 - C_6	1.98	M-L-H	13.08
		V_5 - C_7	1.50	A-H, K- Γ -M	13.13, 13.57
E_7	15.50	V_{14} - C_8	19.18	Γ -A-H, K- Γ -M	15.47
		V_{13} - C_8	15.03	H-K, Γ -M-L-H	15.38
		V_6 - C_9	5.51	A-H, Γ -M, L-H	15.17, 15.40
(Continues)					

TABLE 7 (Continued)

Structure	Peak position	Transitions	Contribution percentage	Region transitions	Energy
		V ₆ -C ₁₀	3.77	A-H, K-Γ-M, L-H	15.70
		V ₂ -C ₁₂	3.21	A-H, H-H, L-H	15.33
		V ₃ -C ₁₂	2.13	A-H-K-Γ-M, L-H	15.80
		V ₄ -C ₁₁	7.28	A-H-K-Γ, L-L	15.43

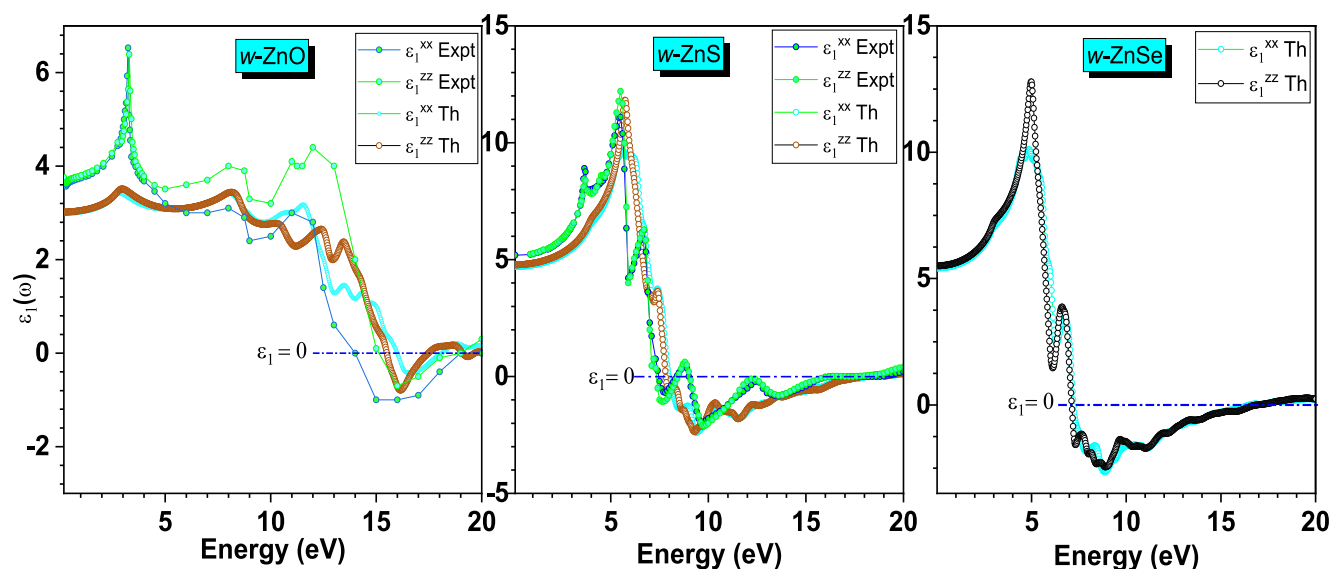


FIGURE 7 (Experimental and theoretical) Real part of the dielectric function for incident radiations (xx) and (zz), for the w-ZnCh compounds. Experimental data from Addachi et al. [41].

indicates that a relative loss anisotropy occurs in the compounds under study. The fast electrons traversing a homogeneous dielectric material are presented by the first intense fine-structure peculiarity in the calculated EELF curve and its localisation associated to the plasma energy $\hbar\omega_p$. Therefore, the plasma resonance manifests itself as two fine-structure peculiarities detected in w-ZnO and three ones in both w-ZnS and w-ZnSe. First of all, in REELS technique, the intensity of bulk plasmon ($\hbar\omega_p$) increases with increasing the excitation energy while the intensity decreases in the case of surface plasmons ($\hbar\omega_s$). Furthermore, the major interband transitions occur as small peaks beyond 10 eV. We observed distinctly bulk plasmon peaks at 18, 19.7 and 14.6 eV for the ZnO, ZnS and ZnSe samples, respectively. The calculation results that correspond well to the REELS measurements which are highlighted by bold font in Tables 2–7. Further details about ZnCh (Ch: O, S and Se) electronic features and their theoretical and experimental assignments are reported in Table 9.

As a comparison between the REELS results recorded in this current study and other experimental finding made by other authors [63–67] indicate a close agreement between the reported peak positions. The slight deviation of our data from

the values reported by other researchers can be explained by the spectrometer energy resolutions, quality of synthesised samples being investigated, performance of excitation sources, VL etc.

4.2 | PLS measurements

The photoluminescence spectroscopy (PLS) is a very powerful technique to characterise defects in semiconductors and insulators. In Figure 17, using this powerful technique, the main peaks of the PLS spectra (and/or) curves of their deconvolutions for the ZnCh samples are presented. The PLS spectra, in fact, traduce the process of the electronic transition between the energetic levels formed in the optical band gap [56, 68]. The luminescence of real materials is typically governed by such factors as interfaces, impurities, vacancies, interstitials, anti-sites, dislocations and so on. These factors influence strongly the main optical properties of the compounds compared to the predicted results. Our intention behind chronological order in the achieved experimental analysis is to get treated samples-cleaned surfaces with the UHV apparatus prepared to a following PLS measurements.

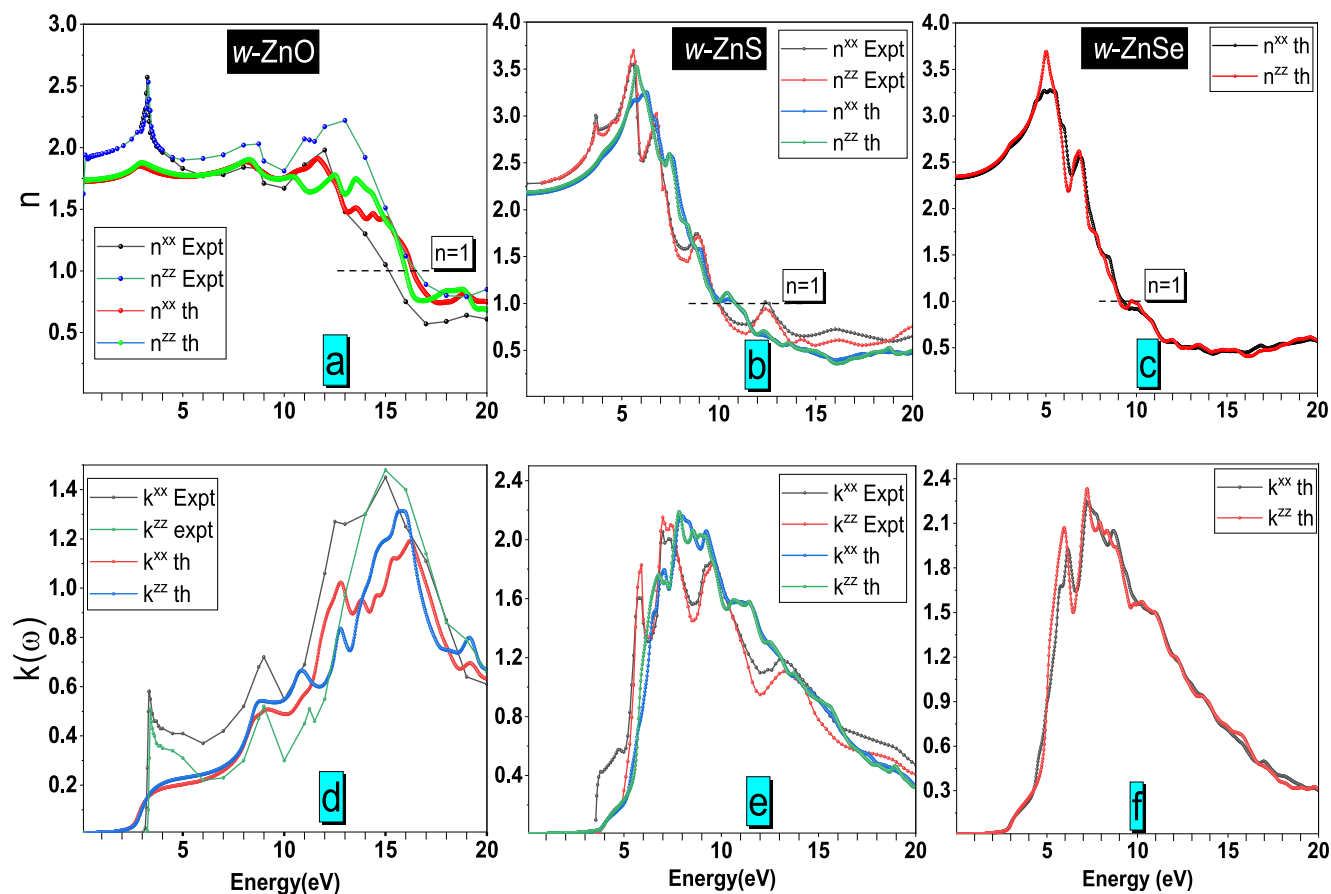


FIGURE 8 (a–c) and (d–f) display the photon energy dependent refractive index $n(\omega)$ and the attenuation coefficient $k(\omega)$ for ZnO, ZnS and ZnSe, respectively.

TABLE 8 Calculated static (dielectric constant $\epsilon_1^{xx}(0)$ and static refractive index $n(0)$ at zero frequency), anisotropy rate A_{opt} and energy for which the dispersion is null $E(n=1)$ for the w-ZnCh compounds in two crystallographic directions. Experimental results headed by (*) estimated from Addachi et al. [41].

	w-ZnO	w-ZnS	w-ZnSe
$\epsilon_1^{xx}(0)$	2.977, 3.759*	4.705, 5.221*	5.420
$\epsilon_1^{zz}(0)$	3.014, 3.670*	4.775, 5.235*	5.505
$n^{xx}(0)$	1.725	2.169, 2.285*	2.328
$n^{zz}(0)$	1.736, 1.625*	2.185, 2.288*	2.346
A_{opt}^{xx}	[0.997; 0.994], [-----; 0.972]*	[0.996; 0.993], [0.998; 0.999]*	[0.997; 0.994], [-----; 0.972]*
A_{opt}^{zz}	[1.003; 1.006], [-----; 1.027]*	[1.004; 1.007], [1.001; 1.000]*	[0.997; 0.994], [-----; 0.972]*
$E(n^{xx}=1)$	16.34, 15.15*	10.87, (9.99, 12.3 and 12.57)*	9.27
$E(n^{zz}=1)$	15.98, 12.76*	10.87, 9.96*	9.08, 9.67

The samples that escaped from the UHV system were installed immediately on the PL sample holder. Therefore, in this framework, we show an important experimental contribution added to the decomposition of the imaginary dielectric tensor together as a complementary tests to explore and display any electronic transitions may be occur in such a compound.

Our experimental results indicate that, according to the Gaussian fitting, all the sub-peaks attributed to some

luminescence possess lower energy than the forbidden region. The main features of the sub-peaks (i.e. their energy location (wavelength), FWHM, peak area and mechanism of electronic transition) are listed in Table 10. The deconvoluted peaks are appropriate to special mechanism defined by electronic transitions between the valence band maximum (VBM^{ax} refer to $V_1(\vec{k})$) and the conduction band minimum (CBMⁱⁿ refer to $C_1(\vec{k})$). These results represent a very useful addition to other

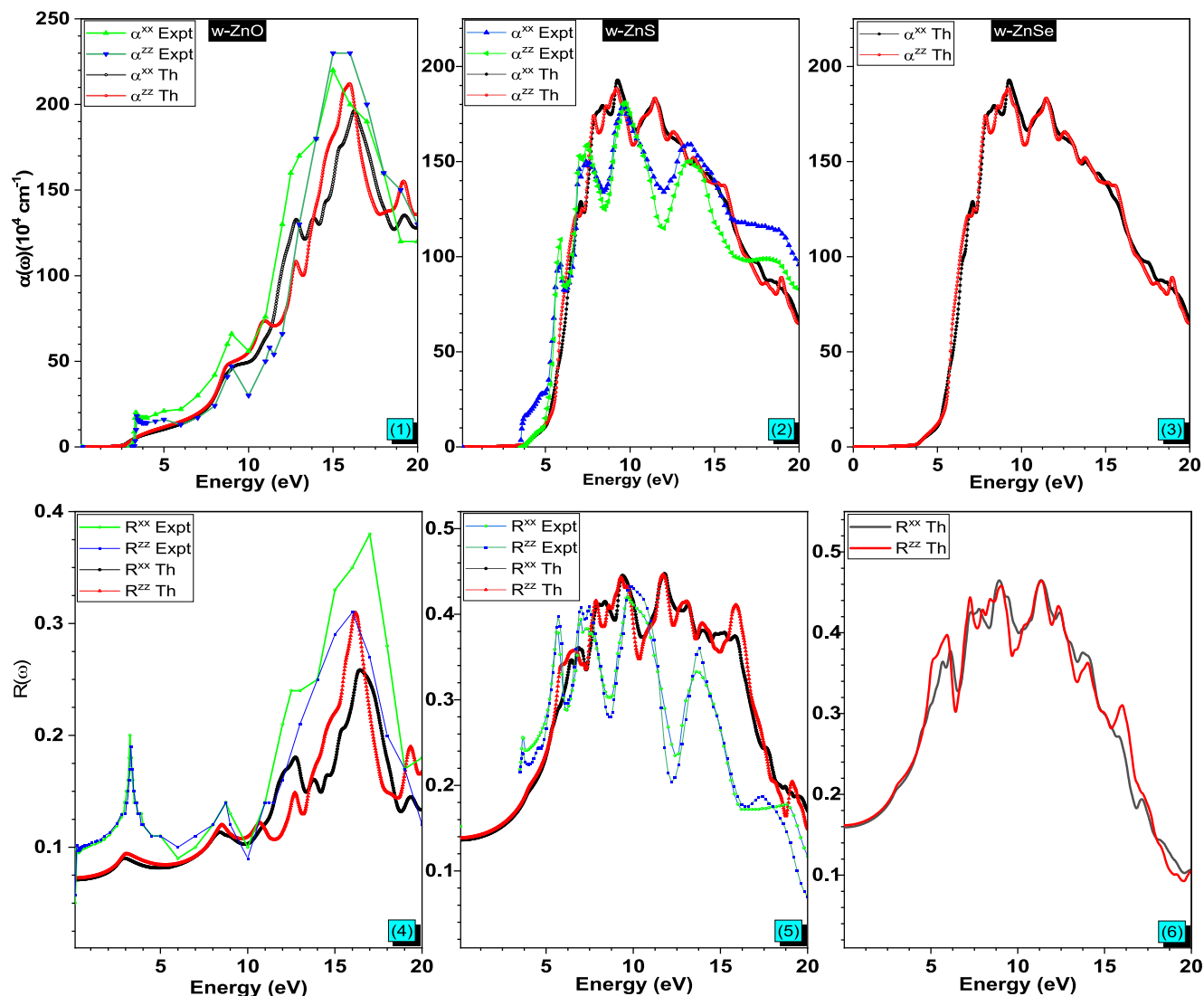


FIGURE 9 The calculated absorption coefficient $\alpha(\omega)$ and static optical reflectivity $R(\omega)$ for w-(ZnO, ZnS and ZnSe) compared with experimental data measured at 300 K and ambient pressure.

finding and allow defining better correlations of the theoretical and experimental data listed in Tables 2–7.

4.3 | UV-visible spectroscopy results

The present ZnCh samples were placed on a rectangular sample holder to be examined by a Shimadzu UV-3101 PC-spectrophotometer for solids with an atmospheric UV–VIS excitation source. The measured spectra (Figure 18) indicate that, the ZnCh samples strongly absorbed photonic irradiations in the UV spectrum range, which is characteristic of the wide gap semiconductors. In particular, the absorbance magnitude relatively changes with the photon excitation wavelength, indicating that ZnO, ZnS and ZnSe samples are very promising compounds for UV sensing and optoelectronic

applications. The main absorption peaks in the recorded spectra are the following: an intense asymmetrical peak at 361 nm (3.43 eV) with a shoulder at 323 nm (3.84 eV) is observed in ZnO thin films. A sharp peak located at 375 nm (3.31 eV) is detected in ZnS, while a rather broad spectrum consisting of three peaks near 322 nm (3.85 eV), 391 nm (3.17 eV) and 443 nm (2.80 eV) is characteristic of the ZnSe sample. Therefore, the absorption peak at 323 nm (3.84 eV) is a common peculiarity of ZnO and ZnSe samples with a deviation near of 1%. The main absorption peak reveals a blue shift in the sequence ZnSe $\rightarrow$ ZnS $\rightarrow$ ZnO which may be attributed to the effect of the increase in chalcogenide electronegativity in such a case. The high absorbance in the UV spectral range could revolutionise the current applications such as UV optical imaging sensors and harvester panels used at the arid areas.

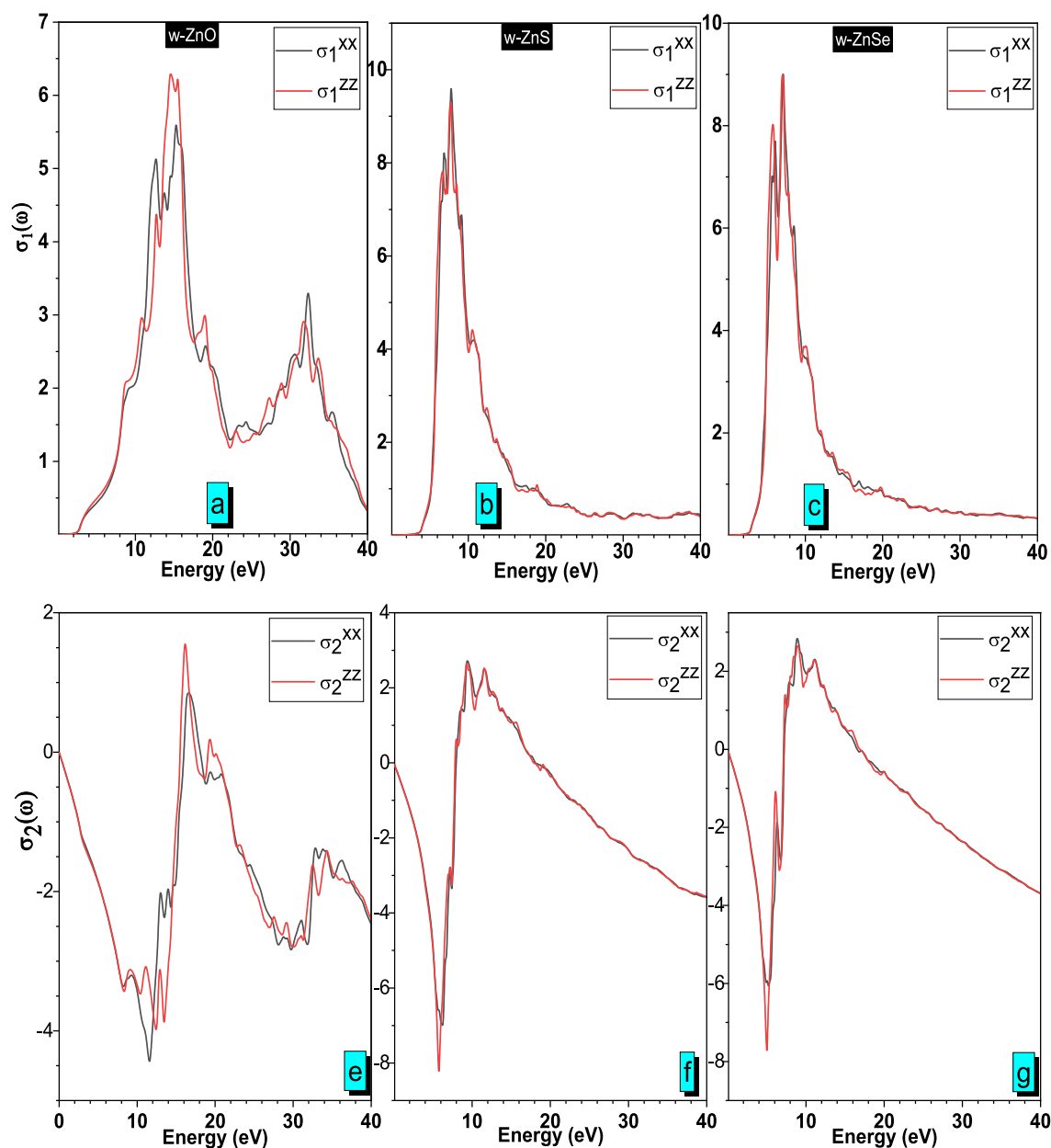


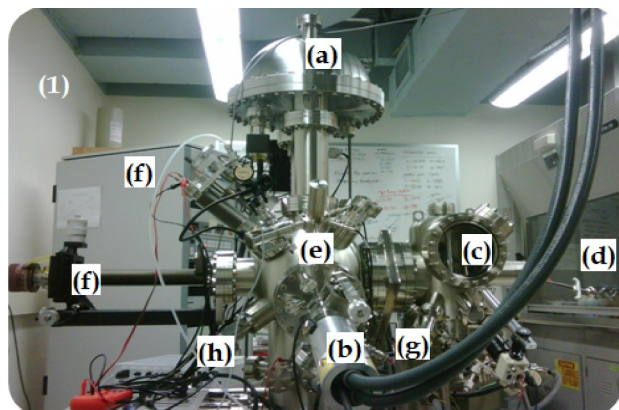
FIGURE 10 Optical photoconductivity $\sigma(\omega)$ with its real part ($\sigma_1(\omega)$) and imaginary part ($\sigma_2(\omega)$) for the w-ZnO, w-ZnS and w-ZnSe compounds.

5 | CONCLUSIONS

In this work, the electronic and optical properties of three Zn bearing mono-chalcogenides (ZnO, ZnS and ZnSe) are investigated in a detailed manner. The electronic band structure dispersion as calculated within the FP-LAPW method at zero pressure employing the TB-mBJ potential for the EXC potential, indicates that w-ZnO, w-ZnS and w-ZnSe are wide direct band gap semiconductors with E_g values of 2.72, 3.87 and 2.88 eV, respectively, which are in good agreement with the available experiments. This means that the use of the TB-mBJ approach for XC potential is very important in the case of DFT calculations of the electronic structure of the ZnCh ($Ch = O, S$ and Se) mono-chalcogenides because it allows

effective exploration of the theoretical optical characteristics of these (and probably many other relative wide band gap semiconductors) without any scissors correction procedure. Based on this approach, it would be possible in future to probe effectively mechanical, vibration, acoustic and other physico-chemical properties of ZnCh ($Ch = O, S$ and Se) and related chalcogenides.

The predictive effective masses indicate the anisotropy in electronic mobility of w-(ZnO, ZnS and ZnSe). The calculated Electron Density Of States (EDOS) spectra show a relative change in bonding character which is related to the electronic distributions change in the upper range of the valence band (V1). The DOS curves reveal different involvements of Zn 3d electronic states in forming bonding



- (a) –Argus Hemi Spherical Analyser (HSA) equipped with 128 channels.
 (b) –X-Ray source DAR 400 (Mg and Al) anodes.
 (c) –Preparation chamber.
 (d) –fume cupboard (thin film preparation and ex-situ cleaning).
 (e) –Analysis chamber.
 (f) –Manipulator (in/out, up/down, right/left and rotation).
 (g) –ISE5 Argon plasma beam.
 (h) –Electron gun (LaB₆ filament).



- (a)–ISE5 Ar⁺ plasma beam.
 (b)– leak valve for Ar gas.

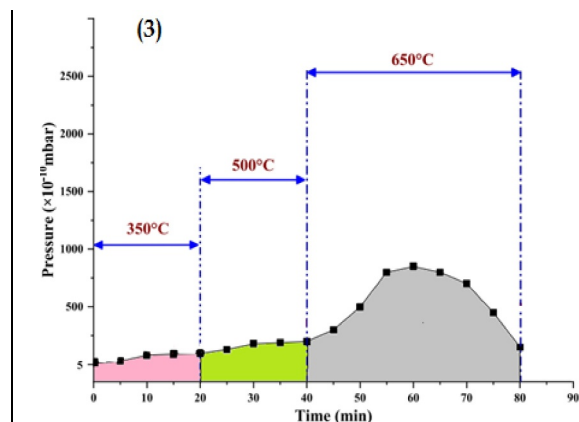


FIGURE 11 (1) Photo of analysis apparatus designed by ScientaOmicron Surface Nano Analysis GmbH Company, Uppsala, Sweden. (2) Side view of Ar⁺ plasma gun and (3) The vacuum level (VL) variations in the analysis apparatus “prep chamber” versus the thermal annealing time with progressive augmented temperatures (350°C – 500°C–650°C).

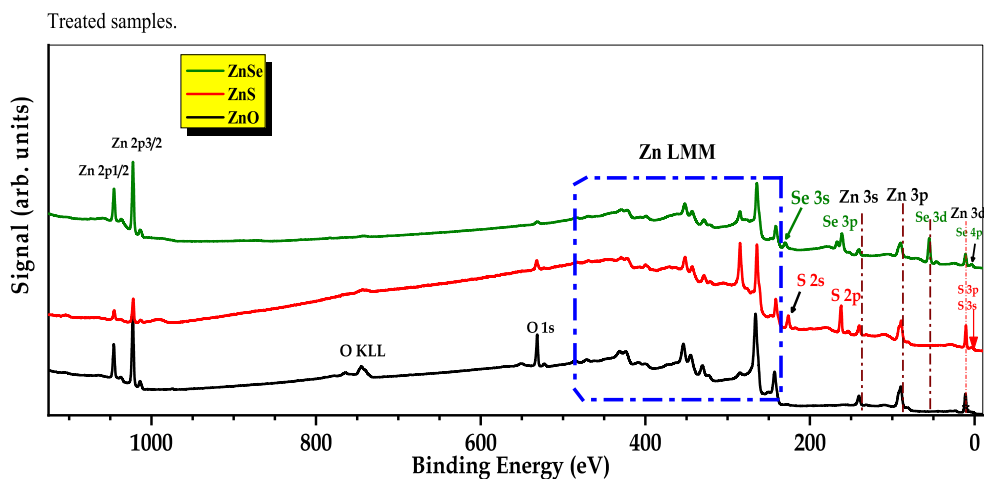


FIGURE 12 X-PES (X-Ray PhotoElectron Spectroscopy) spectra of treated samples ZnO, ZnS and ZnSe obtained with Mg K_α monochromatised radiation (raw data).

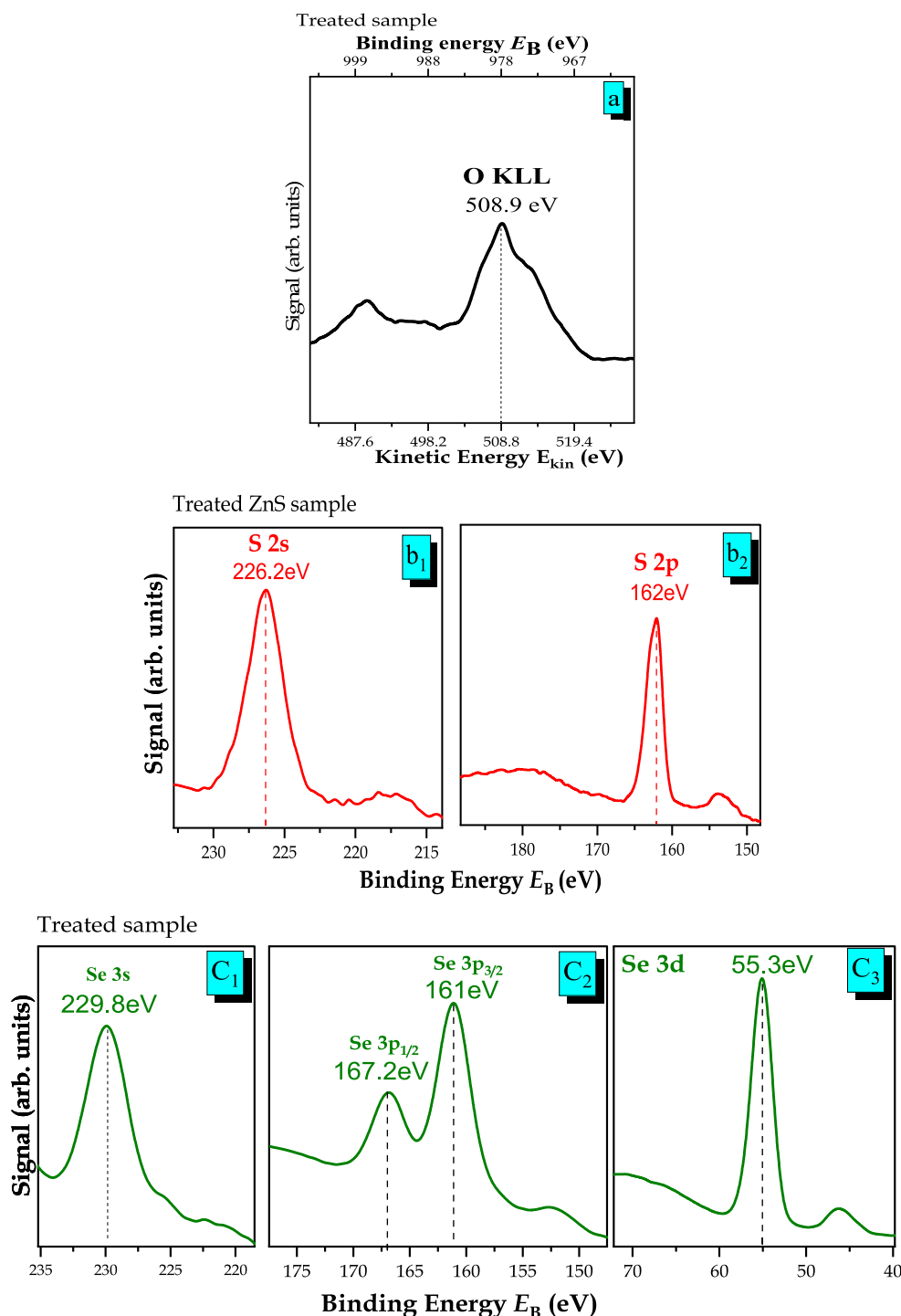


FIGURE 13 The high-resolution (HR) X-PES spectra, show the main peak elements present after Ar⁺ ion bombarded surfaces of ZnCh samples: (a) Oxygen for (Auger O KLL), (b₁ and b₂) sulphur (photoelectrons S 2s and 2p) and (c₁, c₂ and c₃) selenium (photoelectrons Se 3s, 3p_{3/2} and 3d) were detected.

properties when changing neighbouring chalcogen (O, S and Se). The predictive spectra of the real and the imaginary ($\epsilon_1(\omega)$ and $\epsilon_2(\omega)$) parts of the complex dielectric function along the principal crystallographic axes (xx) and (zz) in the hexagonal phase indicate that they are quite different,

revealing the presence of considerable optical anisotropy. According to valence-XPES of the UHV treated samples, the Zn species behaves differently in the ZnCh (Ch = O, S and Se) matrices. The REELS technique proves its ability to probe the most important loss features. The main peaks in

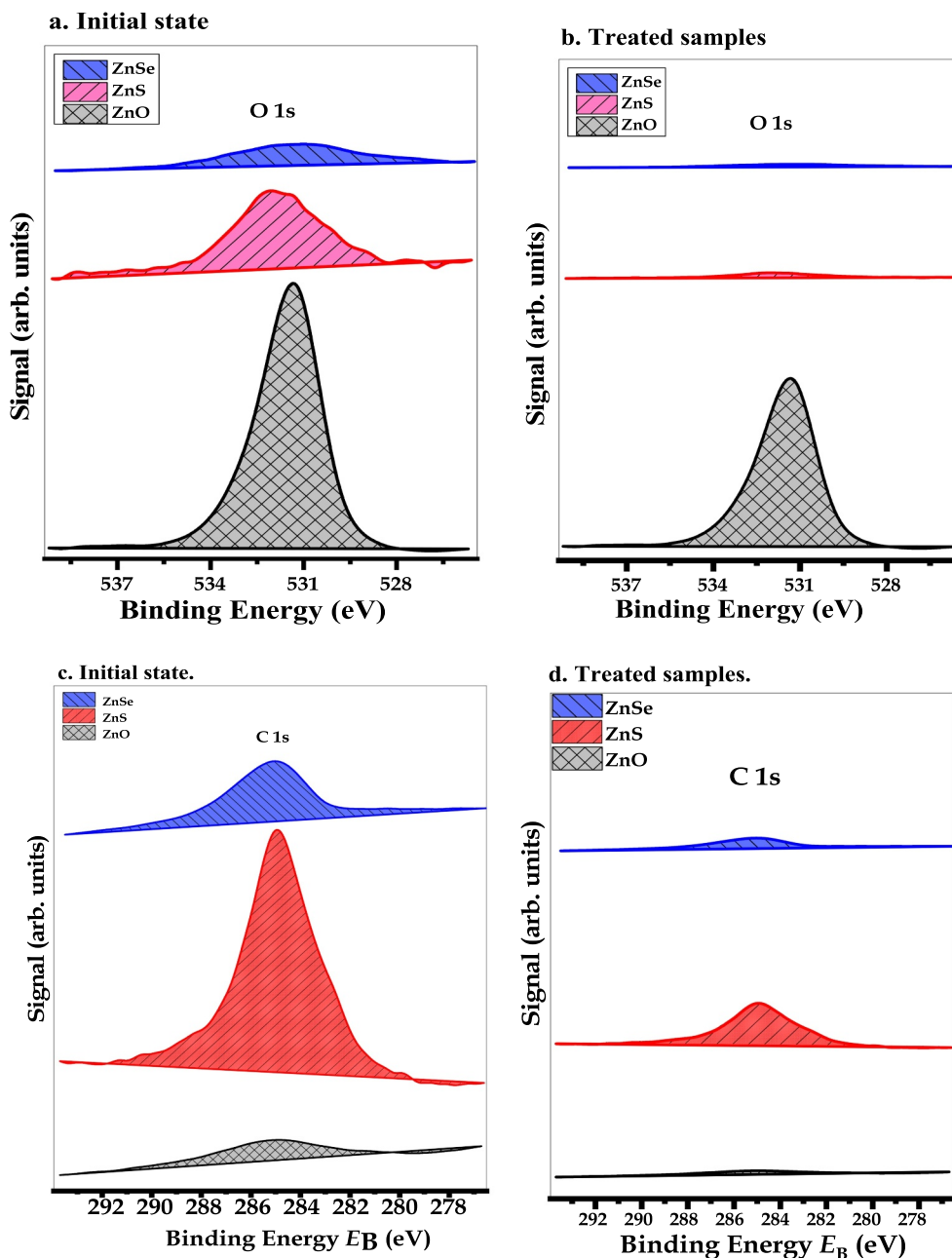


FIGURE 14 High resolution oxygen O 1s and carbon C 1s of ZnCh (Ch: O, S and Se) before (a, c) and after (b, d) UHV treatment.

theoretical EELF curves are confirmed by the other ones in REELS results indicating that the compounds under study possess noticeable loss anisotropy. Our PL measurements at ZnCh (Ch: O, S and Se) compounds unveil details of carrier transfer mechanisms occurring in the optical gap.

The combination of the $\epsilon_2(\omega)$ decompositions and luminescence mechanisms allow us to explore quite number of electronic transitions.

The experimental spectra of the imaginary part $\epsilon_2(\omega)$ of the complex dielectric function are found to be in good

coincidence with the theoretical counterparts. REELS spectroscopy supports well the main features detected in the calculated $\epsilon_2(\omega)$ spectra. The loss features with energies smaller than 10 eV are more pronounced in the REELS spectra as compared to the calculated data. The PLS analysis combined with data on the electronic band structure and the decomposition of the imaginary part of the dielectric function serve us to determine the amount of the structural defects and enable researchers to identify the microscopic origin of the electronic inter band transitions that may occur in such materials. The

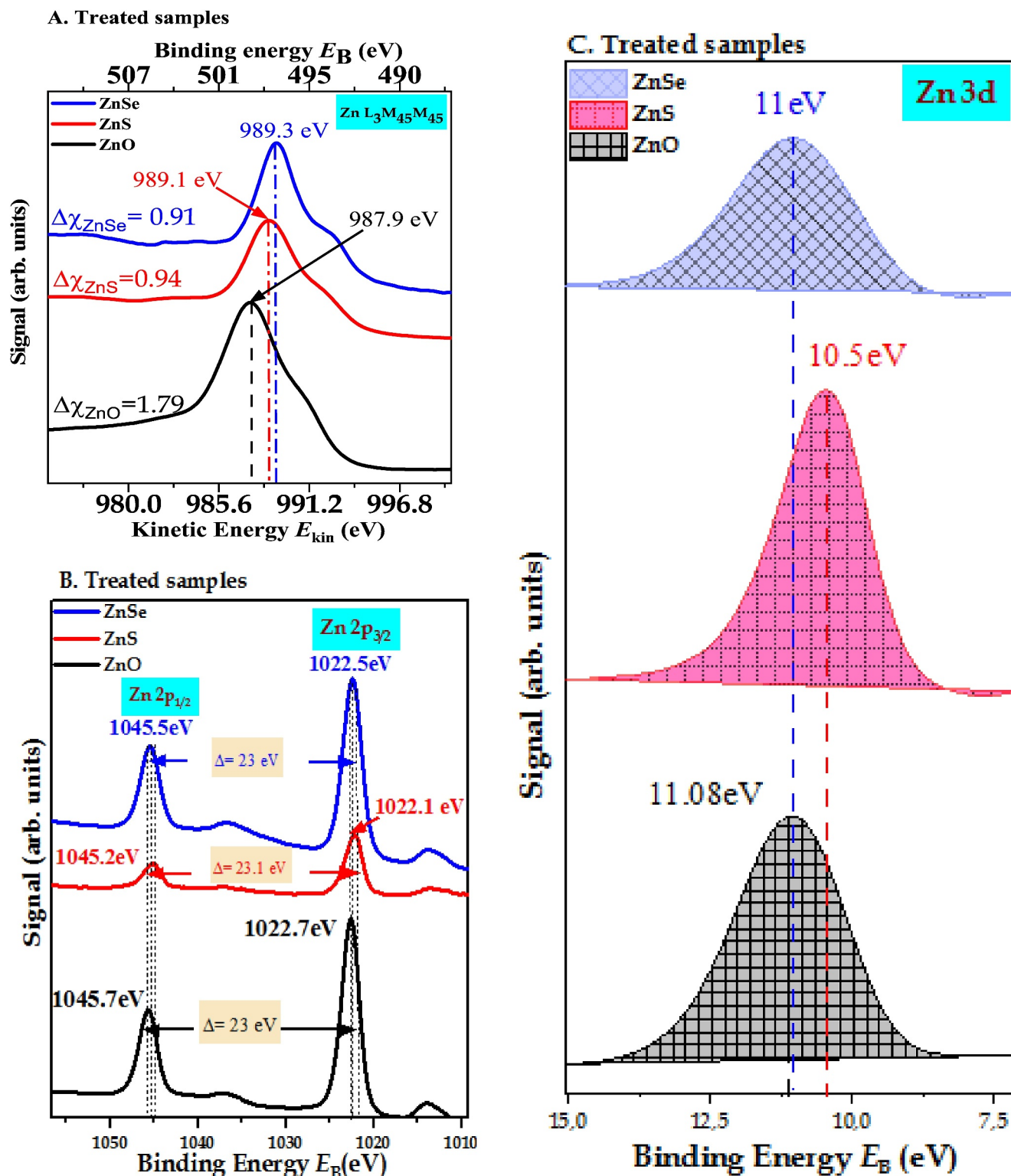


FIGURE 15 A: Well resolved Zn $L_3M_{45}M_{45}$ Auger transition from X-AES (Auger Electron induced by X-Ray excitation) of the treated samples, B and C: the well resolved photoemissions (Zn $2p_{1/2}$ and Zn $2p_{3/2}$) and Zn 3d signals.

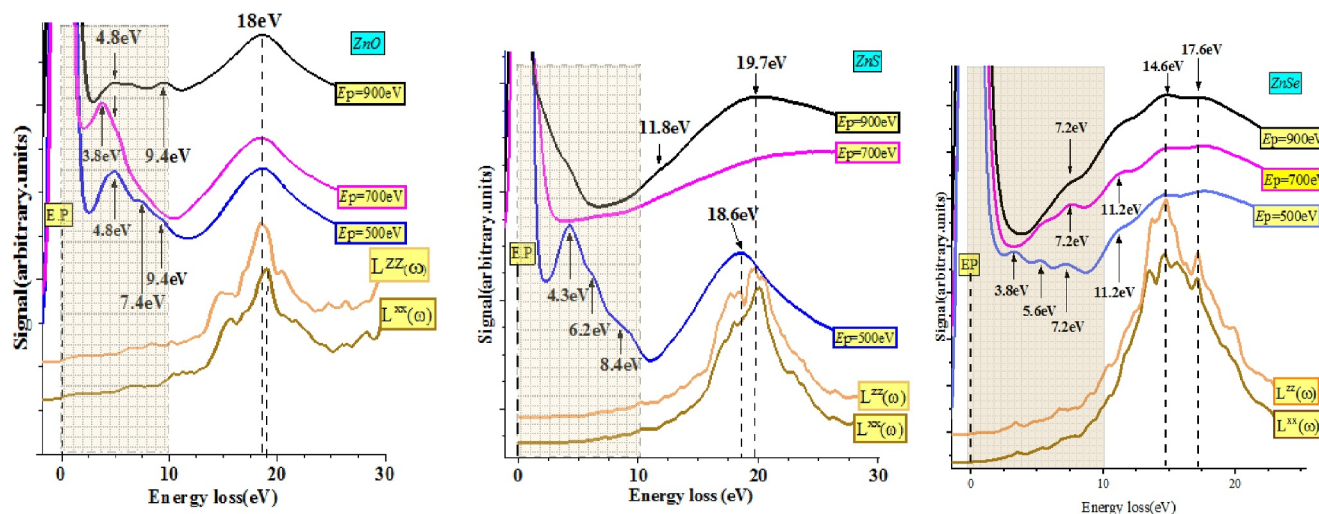


FIGURE 16 The REELS and EELF spectra for treated $ZnCh$ ($Ch=O, S$ and Se) compounds. The REELS spectra recorded at different primary energy of ($EP=900$ eV, $EP=700$ eV and $EP=500$ eV). (EP) refers to the elastic peak with zero loss electron energy.

TABLE 9 Different loss peaks P_i ($i = 1, 2, \dots, 6$) experimental and theoretical position and their assignments with present work and other results (w -ZnO from Ref. [18, 61]; ZnS and ZnSe from Ref. [62–65]). A from Mokadem et al. Ref. [40]. IT, $\hbar\omega_p$ and $\hbar\omega_s$ refer to interband transition, bulk Plasmon loss and surface Plasmon loss, respectively.

Compound:		Loss peak position (eV)		Comment and assignment: $V_i \rightarrow C_j$; Proposed transition (Present work)
		Present	Other	
ZnO	P_1	3.8	3.3	IT: From (O 2p $\rightarrow$ CB)
	P_2	4.8	4.8	IT: $V_2 \rightarrow C_4$
	P_3	7.4	7.3	IT
	P_4	9.4	9.5	IT: From (O 2p $\rightarrow$ Zn 3s)/from: $V_4 \rightarrow C_2$
	P_5	18	18.7	$L^{ZZ}(\omega)_{\max}$, ($\hbar\omega_p + \hbar\omega_s$) IT: from ($V_4 \rightarrow C_2$ and $V_8 \rightarrow C_9$)
ZnS	P_1	4.3	4.5	IT
	P_2	6.2	---	IT: $V_2 \rightarrow C_2$
	P_3	8.4	8.3	IT: From ($V_1 \rightarrow C_7$, $V_1 \rightarrow C_5$, $V_4 \rightarrow C_2$ and $V_4 \rightarrow C_4$)
	P_4	18.6	18.0	Bulk plasmon ($\hbar\omega_p$)
	P_5	19.7	---	$L^{ZZ}(\omega)_{\max}$
ZnSe	P_1	3.8	3.8	IT
	P_2	5.6	5.7	IT: $V_4 \rightarrow C_2$
	P_3	7.2	7.9	IT: ($V_4 \rightarrow C_3$ and $V_2 \rightarrow C_4$)
	P_4	11.2	---	Surface plasmon ($\hbar\omega_s$)
	P_5	14.7	14.9	IT/ $L^{ZZ}(\omega)_{\max}$
	P_6	17.6	17.1	Bulk plasmon ($\hbar\omega_p$)

Note: The bold values in theoretical section (VIZ. Gathered in tables are in well coincidence with the experimental ones that collected from UHV REELS technique).

strong UV colour absorbance confirms the wide band gaps of the $ZnCh$ ($Ch: O, S$ and Se) compounds. The present results feature that, the $ZnCh$ compounds are very suitable candidates for harvesting solar photons in the arid area and promising UV bio-sensors. Furthermore, anisotropy behaviours and peculiar

energy positions/intensities/shapes of the main optical coefficients allow suggesting these compounds to be effectively used in the visible-to-ultra-violet spectral range sensing, for photo-conducting cells, in luminescent and optoelectronic devices.

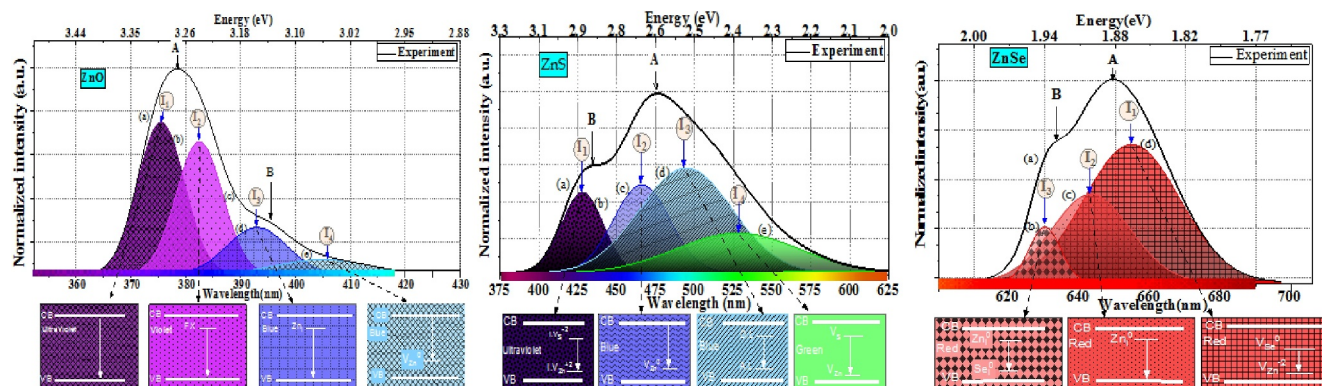


FIGURE 17 Gaussian deconvolution of the RT photoluminescence spectra recorded after 5 min exiting sample from UHV analysis apparatus. Spectra of ZnO and ZnS samples could be fitted very well into four sub-peaks, as labelled by I₁–I₄, and into three sub-peaks for ZnSe, as labelled by I₁–I₃.

TABLE 10 The deconvoluted PLS peaks energy (wavelength), full-width-half-maximum (FWHM), peak area and mechanism of electronic transition of (ZnO, ZnS and ZnSe) are estimated and gathered. C_B min refer to the conduction band minimum, V_B max: Valence band maximum, FX : free excitons, Zn_i : zinc interstitials, V_{Zn}^0 : Zinc vacancies zero charged, $I.V_{Zn}^{+2}$: internal V_{Zn}^{+2} vacancies, $I.V_{S}^{-2}$: Internal V_{S}^{-2} vacancies, DL : donor level, AL : acceptor level, V_S : Sulphur vacancies, V_{Zn} : Zinc vacancies, V_{Se}^0 : Selenium vacancies zero charged and V_{Zn}^{-2} : Zinc vacancies double charged.

Material	PL subpeak	Position wavelength (energy)	FWHM (eV)	Area (a.u.) ²	Transition
ZnO	I ₁ (curve b)	375 nm (3.3eV)	10.1	7.4	$[C_B \text{ min} \rightarrow V_B \text{ max}]$
	I ₂ (curve c)	379.2 nm (3.27eV)	10.0	6.5	$[FX \rightarrow V_B \text{ max}]$ Ref. [56] and others therein
	I ₃ (curve d)	394 nm (3.15eV)	13.2	3.0	$[Zn_i \rightarrow V_B \text{ max}]$
	I ₄ (curve e)	405 nm (3.06eV)	20.1	1.5	$[C_B \text{ min} \rightarrow V_{Zn}^0]$
ZnS	I ₁ (curve b)	427.9 nm (2.90eV)	26.9	14.9	$[I.V_{S}^{-2} \rightarrow I.V_{Zn}^{+2}]$
	I ₂ (curve c)	466 nm (2.66eV)	36.5	22.0	$[C_B \text{ min} \rightarrow V_{Zn}^0]$ Ref. [69] and others therein
	I ₃ (curve d)	494.7 nm (2.51eV)	59.7	43.1	$[DL \rightarrow AL]$
	I ₄ (curve e)	527.8 nm (2.35eV)	79.0	21.6	$[V_S \rightarrow V_{Zn}]$
ZnSe	I ₁ (curve d)	663 nm (1.87eV)	32.5	3.8	$[Zn_i^0 \rightarrow Se_i^0]$
	I ₂ (curve c)	652.6 nm (1.90eV)	24.2	2.0	$[Zn_i^0 \rightarrow V_B \text{ max}]$ Ref. [5] and others therein
	I ₃ (curve b)	639.2 nm (1.94eV)	10.0	0.5	$[V_{Se}^0 \rightarrow V_{Zn}^{-2}]$

Note: The bold values in theoretical section (VIZ. Gathered in tables are in well coincidence with the experimental ones that collected from UHV REELS technique).

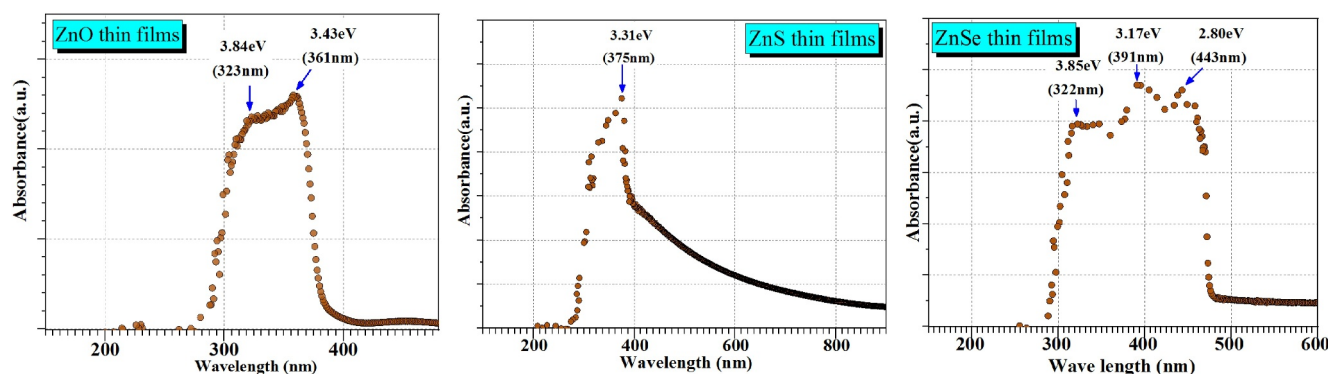


FIGURE 18 The optical absorbance spectra of (ZnO, ZnS and ZnSe) thin films, respectively.

AUTHOR CONTRIBUTIONS

Mohamed Salah Halati: Conceptualization; formal analysis; writing—original draft. Zakia Lounis: Methodology; resources. Oleg Yu. Khyzhun: Funding acquisition; methodology; Yves Caudano: Investigation; software. Kamel Shoush: Validation; writing—review & editing. Prabhu Paramasivam: Software; supervision; writing—review & editing. Sherif Ghoneim: Funding acquisition; validation; writing—review & editing.

ACKNOWLEDGEMENTS

The authors extend their appreciation to Taif University, Saudi Arabia, for supporting this work through the project number (TU-DSPP-2024-14) and are very grateful to the Algerian Ministry of Higher Education in its General Directorate of Scientific Research and Technological Development (DGRSDT) (Algeria) for financial support the Project No. B00L02ES310120200001. Y.C. is a research associate of the Fund for Scientific Research (F.R.S.-FNRS).

CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

All data generated or analysed during this study are included in this published article.

ORCID

Prabhu Paramasivam  <https://orcid.org/0000-0002-2397-0873>

REFERENCES

- Fan, J.C., et al.: p-Type ZnO materials: theory, growth, properties and devices. *Prog. Mater. Sci.* 58(6), 874–985 (2013). <https://doi.org/10.1016/j.pmatsci.2013.03.002>
- Qi, B., Ólafsson, S., Gíslason, H.P.: Vacancy defect-induced d0 ferromagnetism in undoped ZnO nanostructures: controversial origin and challenges. *Prog. Mater. Sci.* 90, 45–74 (2017). <https://doi.org/10.1016/j.pmatsci.2017.07.002>
- Fang, X., et al.: ZnS nanostructures: from synthesis to applications. *Prog. Mater. Sci.* 56(2), 175–287 (2011). <https://doi.org/10.1016/j.pmatsci.2010.10.001>
- Zhang, Qi, et al.: ZnSe nanostructures: synthesis, properties and applications. *Prog. Mater. Sci.* 83, 472–535 (2016). <https://doi.org/10.1016/j.pmatsci.2016.07.005>
- Halati, M.S., et al.: Electronic and optical properties of ZnSe by theoretical simulation TB-mBJ (Tran-Blaha modified Becke johnson) associated to analysis techniques XPS (X-Ray photoelectron spectroscopy); REELS (reflective electron energy loss spectroscopy) and PLS (photoluminescence spectroscopy). *Appl. Surf. Sci.* 566, 150690 (2021). <https://doi.org/10.1016/j.apsusc.2021.150690>
- Georgiadou, D.G., et al.: 100GHz zinc oxide Schottky diodes processed from solution on a wafer scale. *Nature Electronics* 3(11), 718–725 (2020). <https://doi.org/10.1038/s41928-020-00484-7>
- Abdus Subhan, Md, Neogi, N., Choudhury, K.P.: Industrial manufacturing applications of zinc oxide nanomaterials: a comprehensive study. *Nanomanufacturing* 2(4), 265–291 (2022). <https://doi.org/10.3390/nanomanufacturing2040000>
- Liu, J.-C., et al.: Fabrication and characterization of high-sensitivity underwater acoustic multimedia communication devices with thick composite PZT films. *J. Sens.* 1–7 (2017)
- Zhang, Y., Hu, M., Wang, Z.: Enhanced performances of p-Si/n-ZnO self-powered photodetector by interface state modification and pyro-phototronic effect. *Nano Energy* 104630– (2020)
- Ahmad, R., et al.: High performance cholesterol sensor based on ZnO nanotubes grown on Si/Ag electrodes. *Electrochem. Commun.* 38, 4–7 (2014). <https://doi.org/10.1016/j.elecom.2013.10.028>
- Lancellotti, L., et al.: Effects of different graphene dopants on double antireflection coatings/graphene/ n -silicon heterojunction solar cells. *Thin Solid Films* 646, 21–27 (2017). S0040609017308544–. <https://doi.org/10.1016/j.tsf.2017.11.018>
- Ding, G., et al.: Design of flexible image sensors: hybridizing ZnSe light-absorbing layer with highly- flexible graphene channel. *IEEE Electron. Device Lett.* 42(2), 236–239 (2021). <https://doi.org/10.1109/led.2020.3048947>
- Liu, J., et al.: Real-time protein detection using ZnO nanowire/thin film bio-sensor integrated with microfluidic system. 2008 58th Electronic Components and Technology Conference, 1317–1322 (2008). <https://doi.org/10.1109/ectc.2008.4550146>
- Alsebaie, D.M., et al.: Ellipsometric study of optical properties of Sm-doped ZnO thin films Co-deposited by RF-magnetron sputtering. *Optik - International Journal for Light and Electron Optics* 148, 172–180 (2017). S0030402617309348–. <https://doi.org/10.1016/j.ijleo.2017.08.041>
- Sangsefidi, F.S., et al.: Study of hydrogen storage performance of ZnO–CeO2 ceramic nanocomposite and the effect of various parameters to reach the optimum product. *Int. J. Hydrogen Energy*, S0360319918332816 (2018)
- BrunaLallo da, S., et al.: Increased antibacterial activity of ZnO nanoparticles: influence of size and surface modification. *Colloids Surf. B Biointerfaces*, S0927776519300876 (2019)
- Vijayan, S., et al.: Investigation of structural, optical and antibacterial activity of ZnS nanoparticles. *J. Cluster Sci.* 32(6), 1601–1608 (2020). <https://doi.org/10.1007/s10876-020-01923-3>
- Chennai Viswanathan, P., et al.: Deep learning for enhanced fault diagnosis of monoblock centrifugal pumps: spectrogram-based analysis. *Machines* 11(9), 874 (2023). <https://doi.org/10.3390/machines11090874>
- Boutaiba, F., et al.: Polytypism in ZnS, ZnSe, and ZnTe: first-principles study. *Phys. Rev. B* 89(24), 245308 (2014). <https://doi.org/10.1103/physrevb.89.245308>
- Adel, R., et al.: Nanocomposite of CuInS/ZnS and nitrogen-doped graphene quantum dots for cholesterol sensing. *ACS Omega* 6(3), 2167–2176 (2021). <https://doi.org/10.1021/acsomega.0c05416>
- Chandra Patel, P., Srivastava, N., Srivastava, P.C.: Synthesis of wurtzite ZnS nanocrystals at low temperature. *J. Mater. Sci. Mater. Electron.* 24(10), 4098–4104 (2013). <https://doi.org/10.1007/s10854-013-1367-z>
- Senthilkumar, K., et al.: Wurtzite ZnSe quantum dots: synthesis, characterization and PL properties. *J. Mater. Sci. Mater. Electron.* 24(2), 692–696 (2013). <https://doi.org/10.1007/s10854-012-0796-4>
- Blaha, P., et al.: WIEN2k: an augmented plane wave +Local orbitals program for calculating crystal properties. *Karlheinz Schwarz Techn, Universitat, Wien, Austria* (2013). ISBN:3-950131-1-2
- Blaha, P., et al.: WIEN2k: an APW+lo program for calculating the properties of solids. *J. Chem. Phys.* 152(7), 074101 (2020). <https://doi.org/10.1063/1.5143061>
- Tran, F., Blaha, P.: Accurate band gaps of semiconductors and insulators with a semilocal exchange-correlation potential. *Phys. Rev. Lett.* 102(22), 226401 (2009). <https://doi.org/10.1103/physrevlett.102.226401>
- Koller, D., Tran, F., Blaha, P.: Merits and limits of the modified Becke-Johnson exchange potential. *Phys. Rev. B* 83(19), 195134 (2011). <https://doi.org/10.1103/physrevb.83.195134>
- Sai, S.A., et al.: Transfer learning based fault detection for suspension system using vibrational analysis and radar plots. *Machines* 11(8), 778 (2023). <https://doi.org/10.3390/machines11080778>
- Wang, Z.L., Cowley, J.M.: Reflection electron energy loss spectroscopy (reels): a technique for the study of surfaces. *Surf. Sci.* 193(3), 501–512 (1988). [https://doi.org/10.1016/0039-6028\(88\)90449-9](https://doi.org/10.1016/0039-6028(88)90449-9)

29. Anpo, M., Che, M.: Applications of photoluminescence techniques to the characterization of solid surfaces in relation to adsorption, catalysis, and photocatalysis. *Adv. Catal.*, 119–257 (1999). [https://doi.org/10.1016/s0360-0564\(08\)60513-1](https://doi.org/10.1016/s0360-0564(08)60513-1)
30. Lotfy, H.M., Saleh, S.S.: Recent development in ultraviolet spectrophotometry through the last decade (2006–2016): a review. *Int. J. Pharm. Pharmaceut. Sci.* 8(10), 40 (2016). <https://doi.org/10.22159/ijpps.2016v8i10.13537>
31. <http://susi.theochem.tuwien.ac.at>
32. Monkhorst, H.J., Pack, J.D.: Special points for Brillouin-zone integrations. *Phys. Rev. B* 13(12), 5188–5192 (1976). <https://doi.org/10.1103/physrevb.13.5188>
33. Nourbakhsh, Z.: Structural, electronic and optical properties of ZnX and CdX compounds (X=Se, Te and S) under hydrostatic pressure. *J. Alloys Compd.* 505(2), 698–711 (2010). <https://doi.org/10.1016/j.jallcom.2010.06.120>
34. Hümmer, K.: Interband magnetoreflexion of ZnO. *Phys. Status Solidi* 56(1), 249–260 (1973). <https://doi.org/10.1002/pssb.2220560124>
35. Pauling, L.: The nature of the chemical bond. Application of results obtained from the quantum mechanics and from a theory of paramagnetic susceptibility to the structure of molecules. *J. Am. Chem. Soc.* 53(4), 1367–1400 (1931). <https://doi.org/10.1021/ja01355a027>
36. Loganathan, A.S., et al.: Framework of transactive energy market strategies for lucrative peer-to-peer energy transactions. *Energies* 16(1), 6 (2023). <https://doi.org/10.3390/en16010006>
37. Ambrosch-Draxl, C., Sofo, J.O.: Linear optical properties of solids within the fullpotential linearized augmented plane wave method. *Comput. Phys. Commun.* 175(1), 1–14 (2006). <https://doi.org/10.1016/j.cpc.2006.03.005>
38. Kramers, H.A.: The quantum theory of dispersion. *Nature* 114(2861), 310–311 (1924). <https://doi.org/10.1038/114310b0>
39. De, L., Kronig, R.: On the theory of dispersion of X-rays. *J. Opt. Soc. Am.* 12(6), 547 (1926). <https://doi.org/10.1364/josa.12.000547>
40. Mokadem, A., et al.: Investigation of the electron structure of ZnO by the GGA and mBJ calculations associated with the characterization techniques AES and EELS. *Int. J. Mod. Phys. B* 28(11), 1450078 (2014). <https://doi.org/10.1142/s0217979214500787>
41. Addachi, S.: Optical Constants of Crystalline and Amorphous Semiconductors: Numerical Data and Graphical Information. Kluwer Academic, Boston (1999)
42. Alouani, M., Brey, L., Christensen, N.E.: Calculated optical properties of semiconductors. *Phys. Rev. B* 37(3), 1167–1179 (1988). <https://doi.org/10.1103/physrevb.37.1167>
43. Halati, M.S., et al.: Structural, elastic, electronic, optical and anisotropy properties of newly quaternary $\text{Ti}_2\text{HgGeSe}_4$ via DFPT predictions associated to XPS and RS experiments. *Sci. Rep.* 14(1), 16293 (2024). <https://doi.org/10.1038/s41598-024-67231-2>
44. Kalarasse, F., Benneker, B., Mellouki, A.: Optical properties of the filled tetrahedral semiconductors LiMgX (X = N, P and As). *J. Phys. Condens. Matter* 18(31), 7237–7247 (2006). <https://doi.org/10.1088/0953-8984/18/31/018>
45. Kalarasse, F., Benneker, B.: Optical properties of the filled tetrahedral semiconductors LiZnX . X=N, P, and As) 67(8), 1850–1857 (2006). <https://doi.org/10.1016/j.jpcs.2006.04.013>
46. Lambrecht, W.R.L., Rashkeev, S.N.: From band structures to linear and nonlinear optical spectra in Semiconductors 217(1), 599–640 (2000). [https://doi.org/10.1002/\(sici\)1521-3951\(200001\)217:1<599::aid-pssb599>3.0.co;2-o](https://doi.org/10.1002/(sici)1521-3951(200001)217:1<599::aid-pssb599>3.0.co;2-o)
47. Yonghua, D., et al.: First-principles calculations of electronic structures and optical, phononic, and thermodynamic properties of monoclinic α -spodumene. *Ceram. Int.* 43(8), 6312–6321 (2017). <https://doi.org/10.1016/j.ceramint.2017.02.038>
48. Cherrad, D., et al.: Ultra soft pseudo potential investigation of fundamental physical properties of CaXO_3 (X=Sn and Hf) distorted perovskites: a reference study to the perfect perovskites. *Phys. B Condens. Matter* 429, 95–105 (2013). <https://doi.org/10.1016/j.physb.2013.08.002>
49. Magnuson, M., Hultman, L., Högborg, H.: Review of transition-metal diboride thin films. *Vacuum* 110567 (2021)
50. Schroeder, J.L., et al.: Industry-relevant magnetron sputtering and cathodic arc ultra-high vacuum deposition system for in situ x-ray diffraction studies of thin film growth using high energy synchrotron radiation. *Rev. Sci. Instrum.* 86(9), 095113 (2015). <https://doi.org/10.1063/1.4930243>
51. Dorri, S., et al.: Materials & Design, Effects of stoichiometry and individual layer thickness ratio on the quality of epitaxial $\text{CrB}_x/\text{TiB}_y$ superlattice thin films. *Mater. Des.* 228, 111842 (2023). <https://doi.org/10.1016/j.matdes.2023.111842>
52. Shin, C.-S., et al.: Epitaxial growth of metastable δ -TaN layers on $\text{MgO}(001)$ using low-energy, high-flux ion irradiation during ultrahigh vacuum reactive magnetron sputtering. *J. Vac. Sci. Technol. A: Vacuum, Surfaces, and Films* 20(6), 2007–2017 (2002). <https://doi.org/10.1116/1.1513639>
53. Ashikuzzaman Ayon, S., et al.: Improved luminescence and photocatalytic properties of Sm^{3+} -doped ZnO nanoparticles via modified sole-gel route: a unified experimental and DFT+U approach. *J. Rare Earths* 41(4), 550–560 (2023). <https://doi.org/10.1016/j.jre.2022.03.004>
54. Rajagopalan, A., et al.: Multi-objective optimal scheduling of a microgrid using oppositional gradient-based grey wolf optimizer. *Energies* 15(23), 9024 (2022). <https://doi.org/10.3390/en15239024>
55. Qiu, K., et al.: Synthesis of highly twinned ZnSe nanorods for enhancing N_2 electrochemical conversion to NH_3 . *Chem. Commun.* 1039 (2023)
56. Guezoul, M., et al.: Chemical, morphological and optical properties of undoped and Cu-doped ZnO thin films submitted to UHV treatment. *Appl. Surf. Sci.* 146302 (2020)
57. Barreca, D., et al.: ZnO nanoplatelets obtained by chemical vapor deposition, studied by XPS. *Surf. Sci. Spectra* 14(1), 19–26 (2007). <https://doi.org/10.1116/11.20071001>
58. Barreca, D., et al.: Analysis of nanocrystalline ZnS thin films by XPS. *Surf. Sci. Spectra* 9(1), 54–61 (2002). <https://doi.org/10.1116/11.20030117>
59. Shallenberger, J.R., Hellgren, N.: Zinc selenide analyzed by XPS. *Surf. Sci. Spectra* 27(1), 014020 (2020). <https://doi.org/10.1116/6.0000165>
60. Bera, S., et al.: Analysis on binding energy and auger parameter for estimating size and stoichiometry of ZnO nanorods. *Int. J. Spectrosc.* 2012, 1–4 (2012). <https://doi.org/10.1155/2012/371092>
61. L Wong, J.W., et al.: XPS studies of Auger parameter shift of $\text{ZnS}_{1-x}\text{TX}$ alloys. *J. Electron. Spectrosc. Relat. Phenom.* 113(2-3), 215–220 (2001). [https://doi.org/10.1016/s0368-2048\(00\)00430-8](https://doi.org/10.1016/s0368-2048(00)00430-8)
62. Hengehold, R.L., Pedrotti, F.L.: Electron Energy-Loss Spectra of ZnS, ZnSe, and ZnTe. *Phys. Rev. B* 6(8), 3026–3031 (1972). <https://doi.org/10.1103/physrevb.6.3026>
63. Kanimozhi, G., et al.: An effective charger for plug-in hybrid electric vehicles (PHEV) with an enhanced PFC rectifier and ZVS-ZCS DC/DC high-frequency converter. *J. Adv. Transport.* 7840102 (2022). <https://doi.org/10.1155/2022/7840102>
64. Tomoda, T., Mannami, M.-hiko: Characteristic energy loss spectra of II-VI compounds. *J. Phys. Soc. Jpn.* 27(5), 1204–1207 (1969). <https://doi.org/10.1143/jpsj.27.1204>
65. Zhang, Z.H., et al.: Investigation on optical properties of ZnO nanowires by electron energy-loss spectroscopy. *Micron* 37(3), 229–233 (2006). <https://doi.org/10.1016/j.micron.2005.10.016>
66. Langer, D.W., Vesely, C.J.: Electronic core levels of zinc chalcogenides. *Phys. Rev. B* 2(12), 4885–4892 (1970). <https://doi.org/10.1103/physrevb.2.4885>
67. Vesely, C.J., Hengehold, R.L., Langer, D.W.: Levels in the IIB-via compounds. *Phys. Rev. B* 5(6), 2296–2301 (1972). <https://doi.org/10.1103/physrevb.5.2296>

68. Boulenouar, K., et al.: Auger electron spectroscopy, electron energy loss spectroscopy, UV photoelectron spectroscopy, and photoluminescence characterization of In₂O₃ associated to the theoretical calculations based on the generalized gradient approximation and modified Becke Johnson. *J. Phys. Chem. C* 121(15), 8345–8352 (2017). <https://doi.org/10.1021/acs.jpcc.6b11823>
69. Shahi, A.K., et al.: Surfactant assisted surface studies of zinc sulfide nanoparticles. *Appl. Surf. Sci.* 257(23), 9846–9851 (2011). <https://doi.org/10.1016/j.apsusc.2011.06.046>

How to cite this article: Halati, M.S., et al.:

Elucidations of electronic and optical properties of the w-ZnCh (*Ch*=O, S and Se) Compounds: Insights from Ab-initio calculations and spectroscopy measurements. *IET Optoelectron.* 18(6), 188–218 (2024). <https://doi.org/10.1049/ote2.12128>