



Nowotny–Juza NaZnX (X = P, As and Sb) as photovoltaic materials

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Abstract

The electronic band structures of Nowotny–Juza NaZnX (X = P, As and Sb) compounds suggest that the valence band maximum (VBM) and the conduction band minimum (CBM) are located at the center of the Brillouin zone, resulting in a direct band gap of about 1.80, 1.47 and 0.25 eV, respectively. The total and the partial density of states explore the type of orbitals which rule the band gaps and to classify the hybridizations between the orbitals. The VBM is formed mainly by P-p, As-p, Sb-p, Zn-p and Na-p states with substituting P → As → Sb. The CBM of NaZnP is formed by Zn-s, Na-s/p, while the CBM of NaZnAs (NaZnSb) is formed by Zn-s and As-d (Zn-s and Sb-d), one can see that As-d and Sb-d orbitals govern the CBM of NaZnAs and NaZnSb, hence these orbitals rule the energy gaps. It is clear that there exists a strong hybridizations between Na-s/p and As-d states, Zn-s/p and P-p states, Sb-p and Zn-s states and also between Sb-d and Na-s states. The strong hybridization may led to form a strong covalent bonding between these atoms. For more detail and to get deep insight into the electronic structures, the optical properties were investigated. The uniaxial anisotropy and the birefringence values confirm the existence of the considerable anisotropy between the two components of the optical properties. The calculation confirm that these compounds are promising candidates for optoelectronics devices.

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Keywords: Nowotny–Juza compounds; Photovoltaic; Structure properties; Optical properties

1. Introduction

The filled tetrahedral Nowotny–Juza NaZnX (X = P, As and Sb) compounds are direct band gap semiconductors, therefore these compounds are promising candidates for photovoltaic and efficient thermoelectric applications (Wood et al., 1985; Carlsson et al., 1985; Bacewicz et al., 1988; Wei and Zunger, 1986; Kuriyama et al., 1994a,b; Beleanu et al., 2011; Madsen, 2006). There are several experimental and theoretical investigation were reported

for the other Nowotny–Juza compounds for instance LiXY (X = Mg, Zn and Y = N, P, As), LiCdP, LiCdAs and AgMgAs. It was found that LiZnP possess a direct band gap, despite that its binary GaP is indirect band gap semiconductor (Wood et al., 1985). The measured optical gap of LiZnAs founds to be a direct gap of about 1.51 eV at 300 K which is grater than the gap for GaAs (1.42 eV at 300 K) (Ul Haq et al., 2014; Reshak et al., 2013a). Gallium arsenide (GaAs) solar cell shows superior conversion efficiency and radiation resistance when compared to silicon solar cells (Kumar et al., 2004; Deshmukh and Nagaraju, 2005; Minwoo et al., 2013; Davis and Knight, 1975). We should emphasize that there are dearth information concerning the NaZnX (X = P, As and Sb) compounds especially the investigation of the

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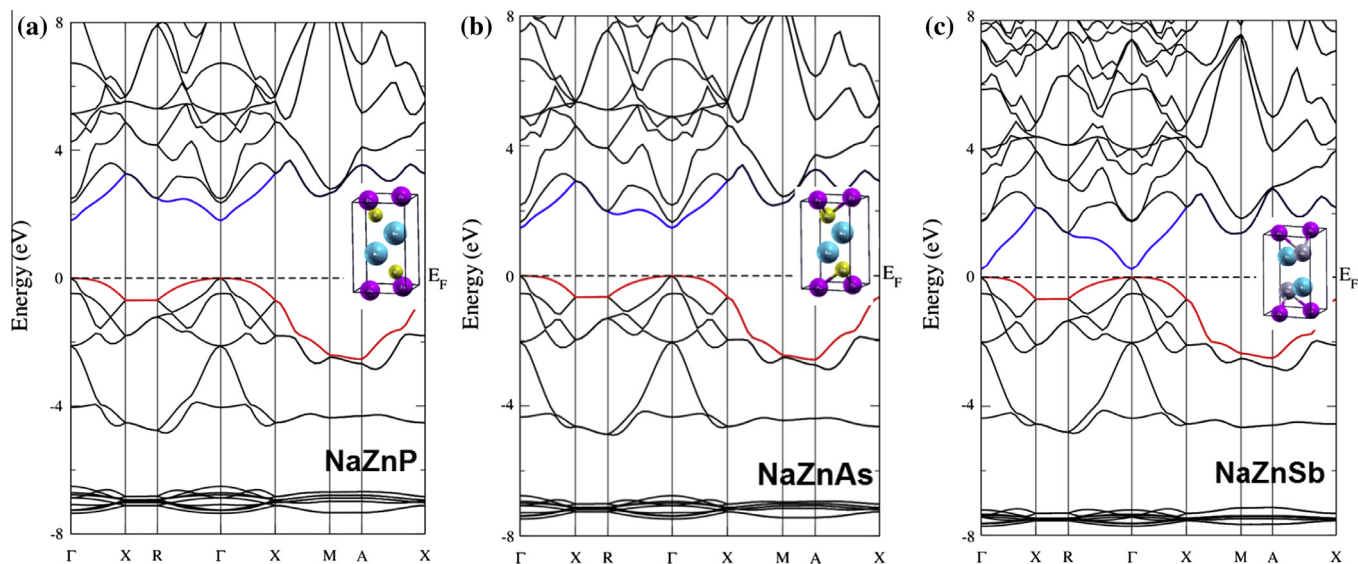


Fig. 1. Calculated electronic band structures of Nowotny–Juzá NaZnX (X = P, As and Sb) compounds using mBJ; (a) NaZnP; (b) NaZnAs; (c) NaZnSb.

Table 1

Calculated energy band gaps, $\varepsilon_1^{\parallel}(0)$, $\varepsilon_1^{\perp}(0)$, $\varepsilon_1^{\text{tot}}(0)$, $\delta\varepsilon(0)$, $R^{\parallel}(0)$, $R^{\perp}(0)$, $n^{\parallel}(0)$, $n^{\perp}(0)$ and $\Delta n(0)$ of Nowotny–Juzá NaZnX (X = P, As and Sb) compounds using mBJ in comparison with previous calculations at ambient pressure and high pressure (α , β , γ -phases).

	NaZnP	NaZnAs	NaZnSb
E_g (eV)	1.80, 0.79 ^a , 0.77 ^b , 1.30 ^c , 0.64 ^d , 0.73 ^e , 0.75 ^f , 0.45 ^g , 1.0 ^h , 0.71 ⁱ , 0.66 ^j , 0.35 ^k , 0.85 ^l , 0.0 ^{m,n}	1.47, 0.44 ^a , 0.39 ^b , 0.79 ^c , 0.163 ^d , 0.0 ^{f,j,o}	0.25, 0.0 ^{a,b,c,d,f,j,o}
$\varepsilon_1^{\parallel}(0)$	6.41	7.40	8.90
$\varepsilon_1^{\perp}(0)$	7.15	8.40	10.50
$\varepsilon_1^{\text{tot}}(0)$	6.78	7.90	9.70
$\delta\varepsilon(0)$	−0.109	−0.126	−0.164
$R^{\parallel}(0)$	0.189	0.214	0.247
$R^{\perp}(0)$	0.207	0.237	0.279
$n^{\parallel}(0)$	2.54	2.72	2.98
$n^{\perp}(0)$	2.69	2.89	3.23
$\Delta n(0)$	0.15	0.17	0.25

^a Reference Charifi et al. (2014) using FPLAPW within LDA.

^b Reference Charifi et al. (2014) using FPLAPW within GGA.

^c Reference Charifi et al. (2014) using FPLAPW within EVGGA.

^d Reference Jaiganesh and Merita (2008) using TB-LMTO method within LDA.

^e Reference Charifi et al. (2014) for α -phase (high pressure phase) using FPLAPW within LDA.

^f Reference Jaiganesh and Merita (2008) for α -phase (high pressure phase) using TB-LMTO method within LDA.

^g Reference Charifi et al. (2014) for α -phase (high pressure phase) using FPLAPW within GGA.

^h Reference Charifi et al. (2014) for α -phase (high pressure phase) using FPLAPW within EVGGA.

ⁱ Reference Charifi et al. (2014) for β -phase (high pressure phase) using FPLAPW within LDA.

^j Reference Jaiganesh and Merita (2008) for β -phase (high pressure phase) using TB-LMTO method within LDA.

^k Reference Charifi et al. (2014) for β -phase (high pressure phase) using FPLAPW within GGA.

^l Reference Charifi et al. (2014) for β -phase (high pressure phase) using FPLAPW within EVGGA.

^m Reference Charifi et al. (2014) for γ -phase (high pressure phase) using FPLAPW within LDA, GGA, EVGGA.

ⁿ Reference Jaiganesh and Merita (2008) for γ -phase (high pressure phase) using TB-LMTO method within LDA.

^o Reference Charifi et al. (2014) for α , β , γ -phases (high pressure phase) using FPLAPW within LDA, GGA, EVGGA.

photovoltaic properties of such important candidates. Recently Charifi et al. (2014) reported a theoretical study on the structural, electronic, elastic and phonon properties of NaZnX (X = P, As and Sb) compounds using the full-potential linear augmented plane wave and pseudopotential plane wave method. They used the generalized-gradient approximation (GGA), the local density approximation (LDA) and Engel–Vosko (EVGGA) formalism, to

calculate the lattice constant, bulk modulus, second-order elastic constants, the electronic band structures and the related total density of states and charge density. They studied three high-pressure phases and found that phase transition pressure occurs from tetragonal to high-pressure phase. Their calculations predict that NaZnSb is a metal in all phases. In 2008, Jaiganesh and Merita, performed first-principles tight-binding linear muffin-tin orbital

(TB-LMTO) method within LDA to calculate the ground-state properties, structural phase stability and pressure dependence of the band gap of the filled tetrahedral Nowotny–Juza NaZnP, NaZnAs, and NaZnSb compounds. The calculation predict that NaZnP, NaZnAs, and NaZnSb compounds are crystallize in the tetragonal Cu_2Sb -type (C38) structure. The authors found three phases α , β and γ when they interchanging the position of the atoms in the zinc-blende structure. Calculation predict that these compounds are more stable in the Cu_2Sb -type structure under ambient conditions, whereas these compounds undergo a structural phase transition from the tetragonal

Cu_2Sb -type to cubic α (or β) phase at high pressure. In the Cu_2Sb -type structure, NaZnP was found to be a direct gap semiconductor, NaZnAs shows a very small direct band gap and NaZnSb was predicted to be a metallic. In additional, the authors reported that in the α and β phases the NaZnP was found to be a direct gap semiconductor, whereas NaZnAs and NaZnSb are found to be semi-metallic. Finally in γ -phase, all the three compounds are found to be metallic.

From above it is clear that the theoretical investigations were performed using LDA, GGA and EVGGA, it is well know that LDA, GGA and EVGGA underestimated the

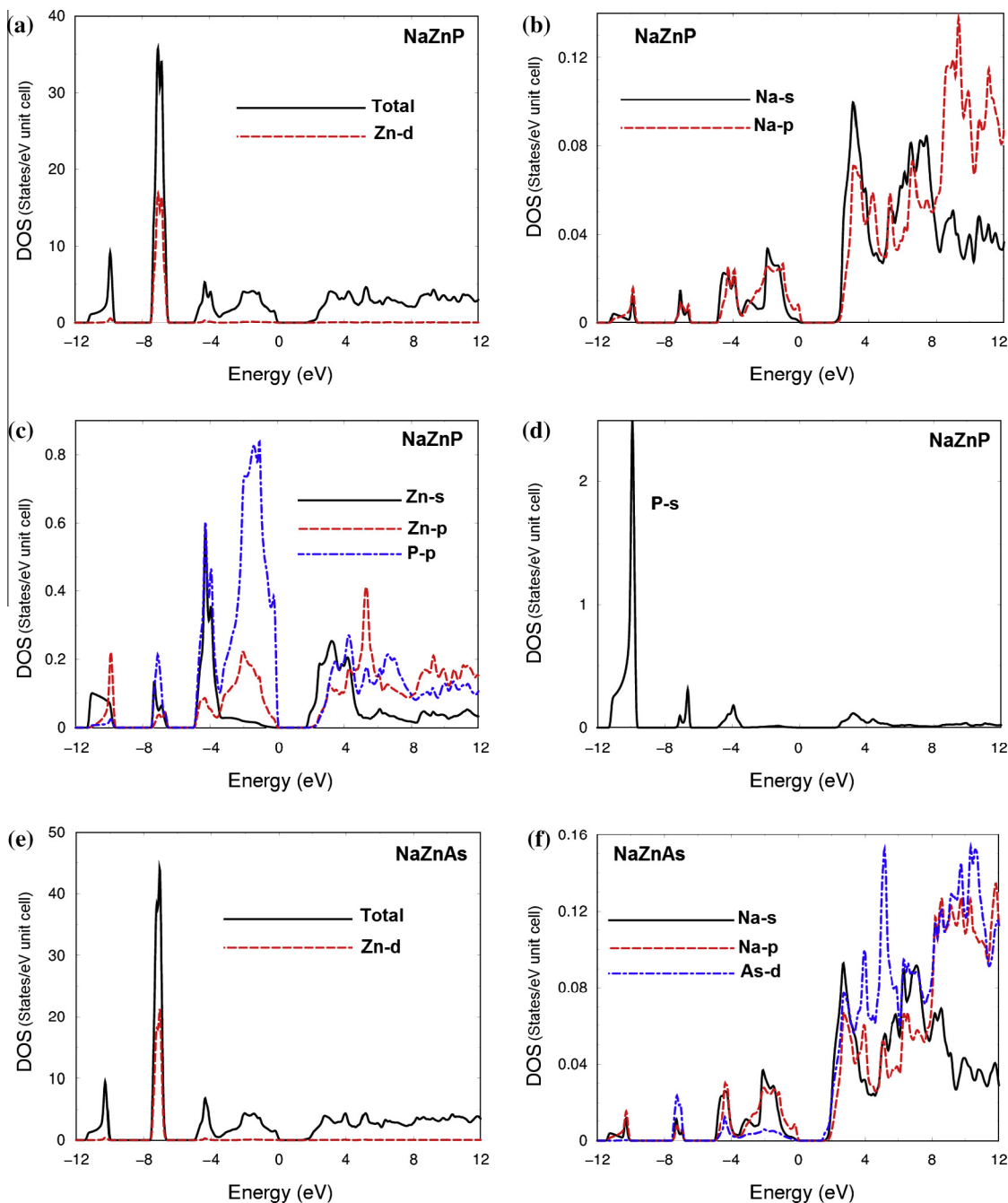


Fig. 2. Calculated total and partial density of states for Nowotny–Juza NaZnX (X = P, As and Sb) compounds using mBJ; (a–d) NaZnP; (e–h) NaZnAs; (i–l) NaZnSb.

energy band gap (Reshak et al., 2013b) therefore, this motivate us to address ourselves for comprehensive theoretical calculation using the state-of-the-art-all-electron full potential linear augmented plane wave (FP-LAPW) method, within the modified Becke–Johnson potential (mBJ) (Tran and Blaha, 2009), which optimizes the corresponding potential for electronic band structure calculations. The mBJ, a modified Becke–Johnson potential, allows the calculation of band gaps with accuracy similar to the very expensive GW calculations (Tran and Blaha, 2009). It is a local approximation to an atomic “exact-exchange” potential and a screening term. The FP-LAPW method has

proven to be one of the most accurate method to calculate the properties of the solid with density functional theory (Gao, 2003; Schwarz 2003).

2. Details of calculation

Based on previous reports (Charifi et al. 2014; Jaiganesh and Merita 2008) which state that the Nowotny–Juza NaZnX (X = P, As and Sb) compounds are more stable in the Cu₂Sb-type structure under ambient conditions. Therefore we focused our interest to comprehensively investigate the ground state properties of these compounds under

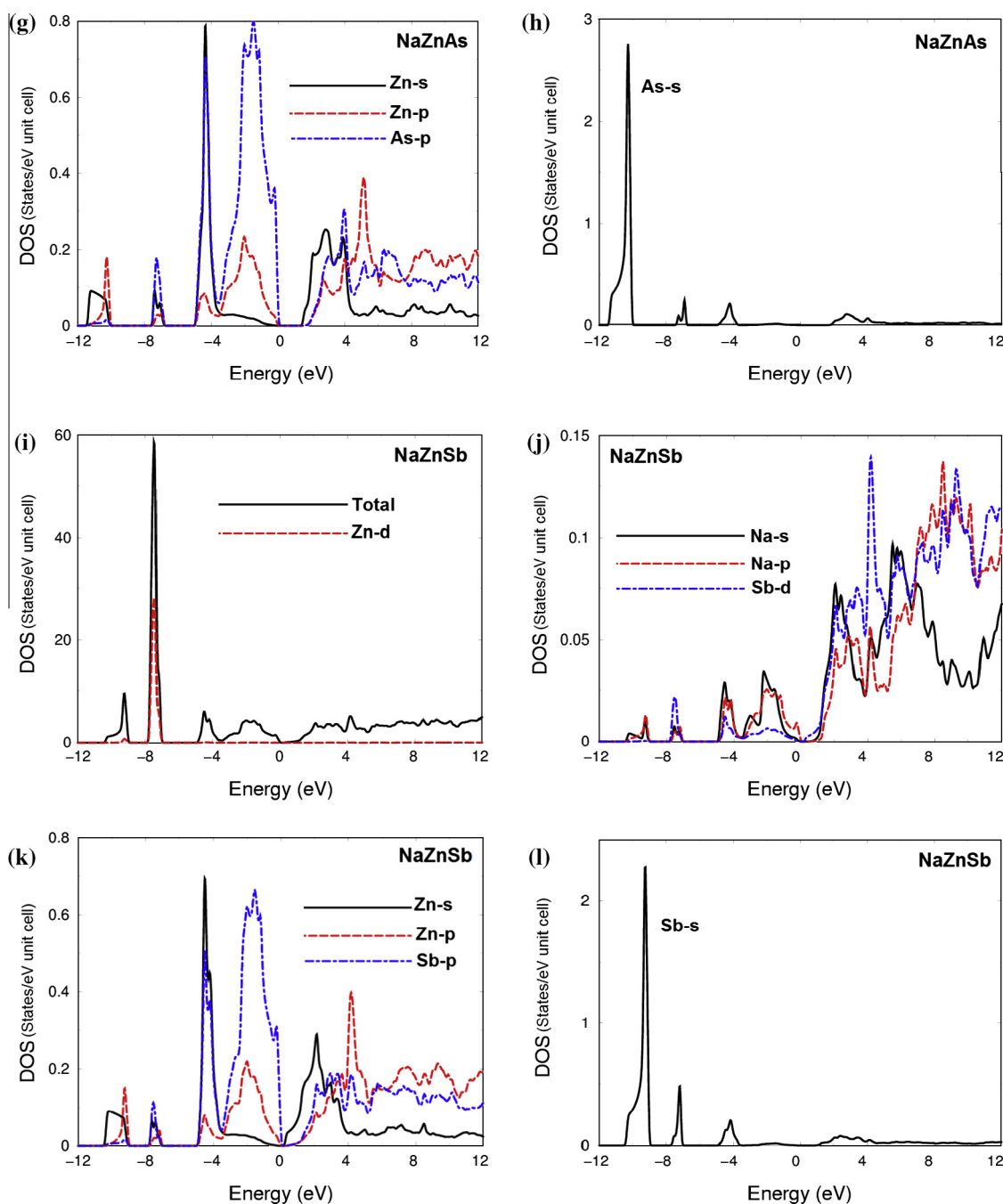


Fig 2. (continued)

ambient conditions. At ambient pressure Nowotny–Juza NaZnX (X = P, As and Sb) compounds crystallizes in tetragonal space group P4/nmm, which is the most stable phase. We have employed the state-of-the-art full potential linear augmented plane wave (FPLAPW) method in a scalar relativistic version as embodied in the WIEN2k code (Blaha et al., 2001) within the recently modified Becke–Johnson potential (mBJ) to perform band structure calculations. We have used a basis of linear APW's to solve the Kohn–Sham equations. The potential and charge density in the muffin-tin (MT) spheres were expanded in spherical harmonics with $l_{max} = 8$ and nonspherical components up to $l_{max} = 6$. In the interstitial region the potential and the charge density were represented by Fourier series. To achieve the self-consistency a mesh of 5000 \bar{k} points in the irreducible Brillouin zone (IBZ) was used. The electronic band structure, density of states, and the optical properties were calculated using very dense \bar{k} meshes of 11560 \bar{k} points in the IBZ. The convergence of the total energy in the self-consistent calculations is taken with respect to the total charge of the system with a tolerance 0.0001 electron charges.

3. Results and discussion

3.1. Electronic band structure and density of states

The electronic band structures of Nowotny–Juza NaZnX (X = P, As and Sb) compounds in the first Brillouin zone were calculated along the high symmetry points as illustrated in Fig. 1(a–c). The figures show that the valence band maximum (VBM) and the conduction band minimum (CBM) are located at the center of the BZ, resulting in a direct band gap of about 1.80, 1.47 and 0.25 eV for NaZnX (X = P, As and Sb), respectively. Substituting P by As cause to push the CB's toward Fermi level (E_F) by around 0.33 eV, while substituting As by Sb led to dramatic changes in the locations and the bandwidths of the CB's, resulting in huge reduction in the band gap of about 1.55 eV with respect to NaZnP. The band gap reduction is attributed to the fact that the atomic radius of Sb (145×10^{-12} m) > As (115×10^{-12} m) > P (100×10^{-12} m), therefore the difference between P and As radius is 15×10^{-12} m which led to small shifts in the CB's toward E_F , whereas the difference between P and Sb radius is 35×10^{-12} m that is the reason behind the huge reduction in the NaZnSb band gap with respect to NaZnAs and NaZnP. We should emphasize that since the electro-negativity difference between P, As and Sb is very small therefore substituting P \rightarrow As \rightarrow Sb will not introduce more peaks in the density of states above the CBM (Joo et al., 2010). Overall the electronic band structures of the three compounds look similar except the band gap reduction when one move from P \rightarrow As \rightarrow Sb. To the best of our knowledge, there are no previous experimental data for the energy band gaps available in literature to make a meaningful comparison. But we can compare our

calculated energy band gaps with previous calculations of Charifi et al. (2014) using FPLAPW within LDA, GGA and EVGGA and also with the calculations of Jaiganesh and Merita (2008) using TB-LMTO method within LDA. These values are listed in Table 1.

In order to investigate the type of orbitals which rule the band gaps and to classify the hybridizations between the orbitals, we investigate the total and the partial density of states as shown in Fig. 3 (a–l). These figures suggest that the VBM is formed mainly by P-p, As-p, Sb-p, Zn-p and Na-p states, as it is clear from Figs. 2 and 3. The CBM of NaZnP is formed by Zn-s, Na-s/p, while the CBM of NaZnAs (NaZnSb) is formed by Zn-s and As-d (Zn-s and Sb-d), one can see that As-d and Sb-d are govern the CBM of NaZnAs and NaZnSb resulting in rule the energy gaps. It is clear that there exists a strong hybridizations between Na-s/p and As-d states, Zn-s/p and P-p states, Sb-p and Zn-s states and also between Sb-d and Na-s states. The strong hybridization may led to form a strong covalent bonding between these atoms.

3.2. Optical properties

The optical properties of solids are a major topic, both in basic research as well as for industrial applications. While for the former the origin and nature of different excitation processes is of fundamental interest, the latter can make use of them in many optoelectronic devices. These wide interests require experiment and theory. The calculations of the frequency dependent dielectric function involve the energy eigenvalues and electron wave functions. These are natural outputs of band structure calculations. Nowotny–Juza NaZnX (X = P, As and Sb) compounds have tetragonal structure with space group P4/nmm. The tetragonal symmetry allows only two dielectric tensor components, which completely characterize the linear optical properties. These are the parallel and the perpendicular components of the imaginary part of the frequency dependent dielectric function $\varepsilon_2^{xx}(\omega)$, $\varepsilon_2^{yy}(\omega)$ and $\varepsilon_2^{zz}(\omega)$, where $\varepsilon_2^{xx}(\omega) = \varepsilon_2^{yy}(\omega) = \varepsilon_2^{\perp}(\omega)$ while $\varepsilon_2^{zz}(\omega) = \varepsilon_2^{\parallel}(\omega)$. We have performed calculations of the imaginary part of the inter-band frequency dependent dielectric function using the expressions (Hufner et al., 1999);

$$\varepsilon_2^{\parallel}(\omega) = \frac{12}{m\omega^2} \int_{BZ} \sum_{nn'} \frac{|P_{nn'}^Z(k)|^2 dS_k}{\nabla \omega_{nn'}(k)} \quad (1)$$

$$\varepsilon_2^{\perp}(\omega) = \frac{6}{m\omega^2} \int_{BZ} \sum_{nn'} \frac{[|P_{nn'}^X(k)|^2 + |P_{nn'}^Y(k)|^2] dS_k}{\nabla \omega_{nn'}(k)} \quad (2)$$

The above expressions are written in atomic units with $e^2 = 1/m = 2$ and $\hbar = 1$. Where $\hbar\omega$ is the photon energy. $P_{nn'}^X(k)$ and $P_{nn'}^Z(k)$ are the X and Z component of the dipolar matrix elements between initial $|nk\rangle$ and final $|n'k\rangle$ states with their eigenvalues $E_n(k)$ and $E_{n'}(k)$, respectively. $\omega_{nn'}(k)$ is the inter-band energy difference

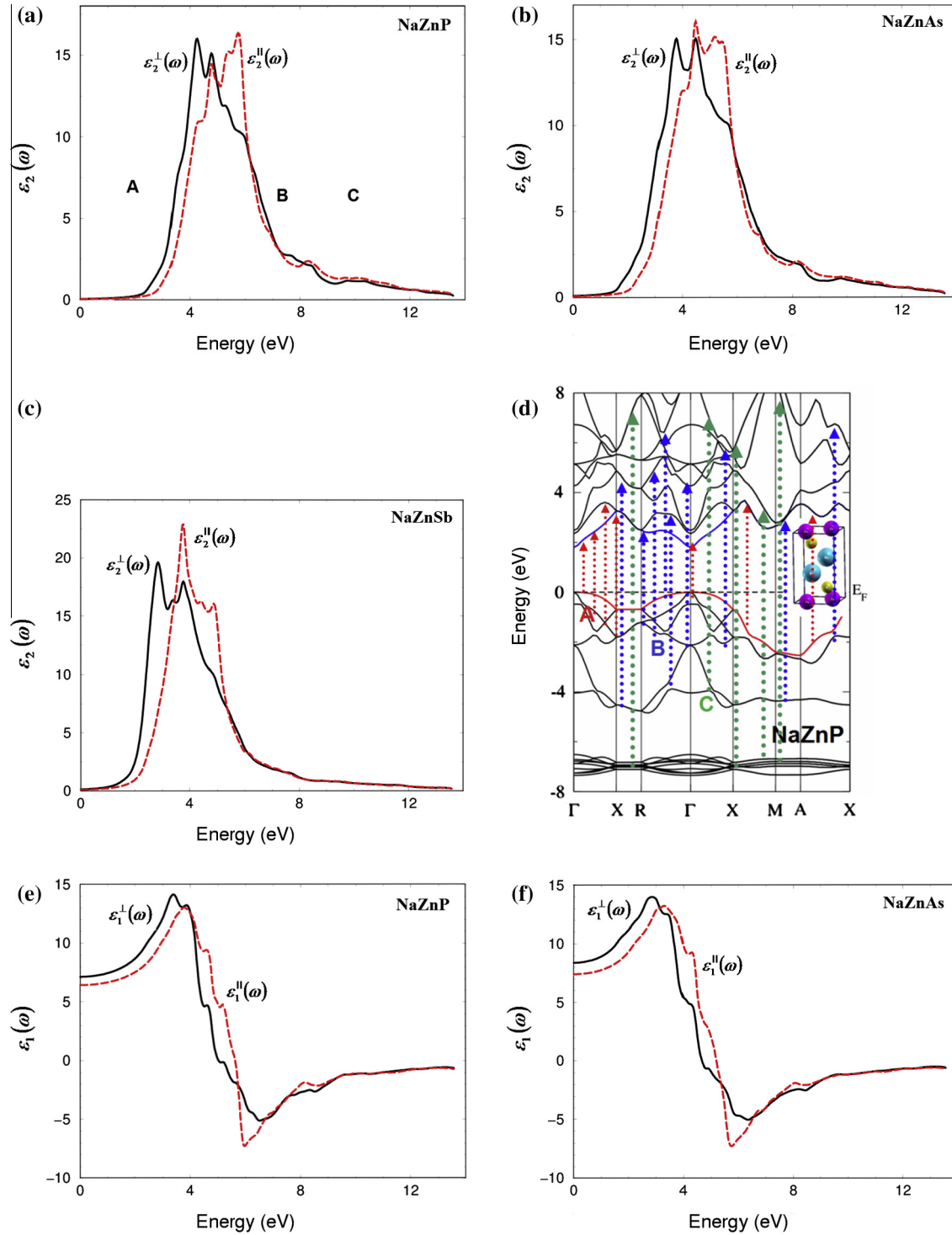


Fig. 3. (a–c) Calculated $\epsilon_2^\perp(\omega)$ (dark solid curve – black color online) and $\epsilon_2^\parallel(\omega)$ (light dashed curve – red color online); (d) the optical transitions depicted on a generic band structure, as prototype we show the optical transitions of NaZnP; (e–g) calculated $\epsilon_1^\perp(\omega)$ (dark solid curve – black color online) and $\epsilon_1^\parallel(\omega)$ (light dashed curve – red color online); (h–j) calculated $R^\perp(\omega)$ (dark solid curve – black color online) and $R^\parallel(\omega)$ (light dashed curve – red color online); (k–m) calculated absorption coefficient $I^\perp(\omega)$ (dark solid curve – black color online) and $I^\parallel(\omega)$ (light dashed curve – red color online). The absorption coefficient in 10^4 s^{-1} ; (n–p) calculated refractive indices $n^\perp(\omega)$ (dark solid curve – black color online) and $n^\parallel(\omega)$ (light dashed curve – red color online); (q–s) Calculated birefringence $\Delta n(\omega)$; (t–v) calculated imaginary part of the optical conductivity $im\sigma^\perp(\omega)$ (dark solid curve – black color online) and $im\sigma^\parallel(\omega)$ (light dashed curve – red color online). The optical conductivity in 10^{15} s^{-1} ; (w–y) calculated real part of the optical conductivity $re\sigma^\perp(\omega)$ (dark solid curve – black color online) and $re\sigma^\parallel(\omega)$ (light dashed curve – red color online). The optical conductivity in 10^{15} s^{-1} . All the optical properties are calculated within mBJ. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

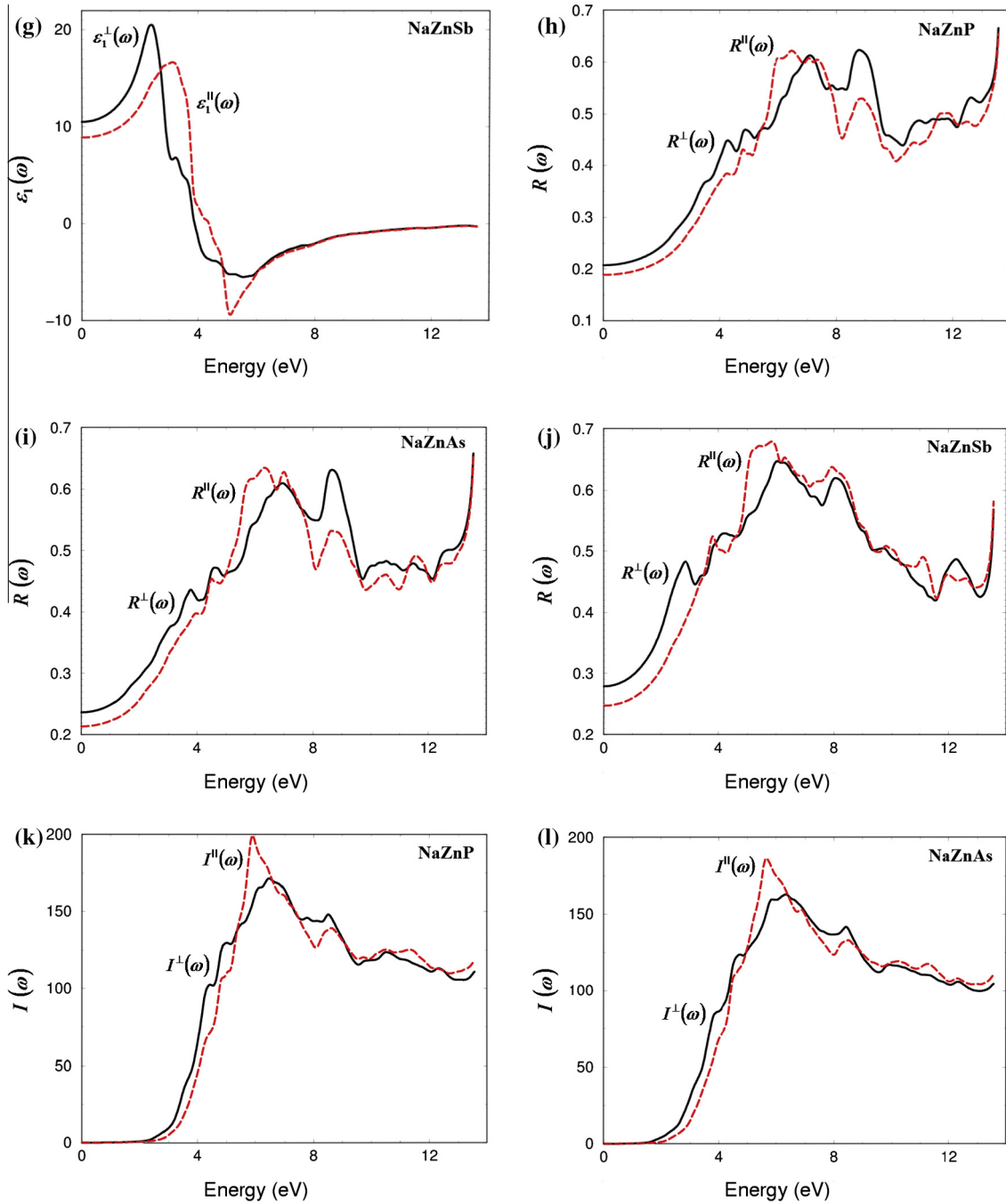


Fig 3. (continued)

$$\omega_{mn'}(k) = E_n(k) - E_{n'}(k) \quad (3)$$

and S_k is a constant energy surface

$S_k = \{k; \omega_{mn'}(k) = \omega\}$. The integral is taken over the first Brillouin zone. The dispersion of the imaginary part of the dielectric function $\varepsilon_2^{\parallel}(\omega)$ and $\varepsilon_2^{\perp}(\omega)$ can be calculated from the momentum matrix elements between the occupied and unoccupied wavefunctions, giving rise to the selection rules.

The calculated $\varepsilon_2^{\parallel}(\omega)$ and $\varepsilon_2^{\perp}(\omega)$ spectra for Nowotny–Juza NaZnX (X = P, As and Sb) compounds are illustrated

in Fig. 3(a–c). Substituting P by As and As by Sb, the optical spectrum shift toward lower energies, confirming our previous finding that the band gap decreases substantially with moving from P → As → Sb. The shifting in the optical spectrum is consistent with our calculated band structure and corresponding density of states. The first critical points (absorption edges) are located at 1.80, 1.47 and 0.25 eV for $\varepsilon_2^{\parallel}(\omega)$ and $\varepsilon_2^{\perp}(\omega)$ of NaZnP, NaZnAs and NaZnSb, respectively. The peak heights decrease with substituting P by As then it increases when As substituted by Sb. The analysis of $\varepsilon_2(\omega)$ curve shows that the investigated compounds

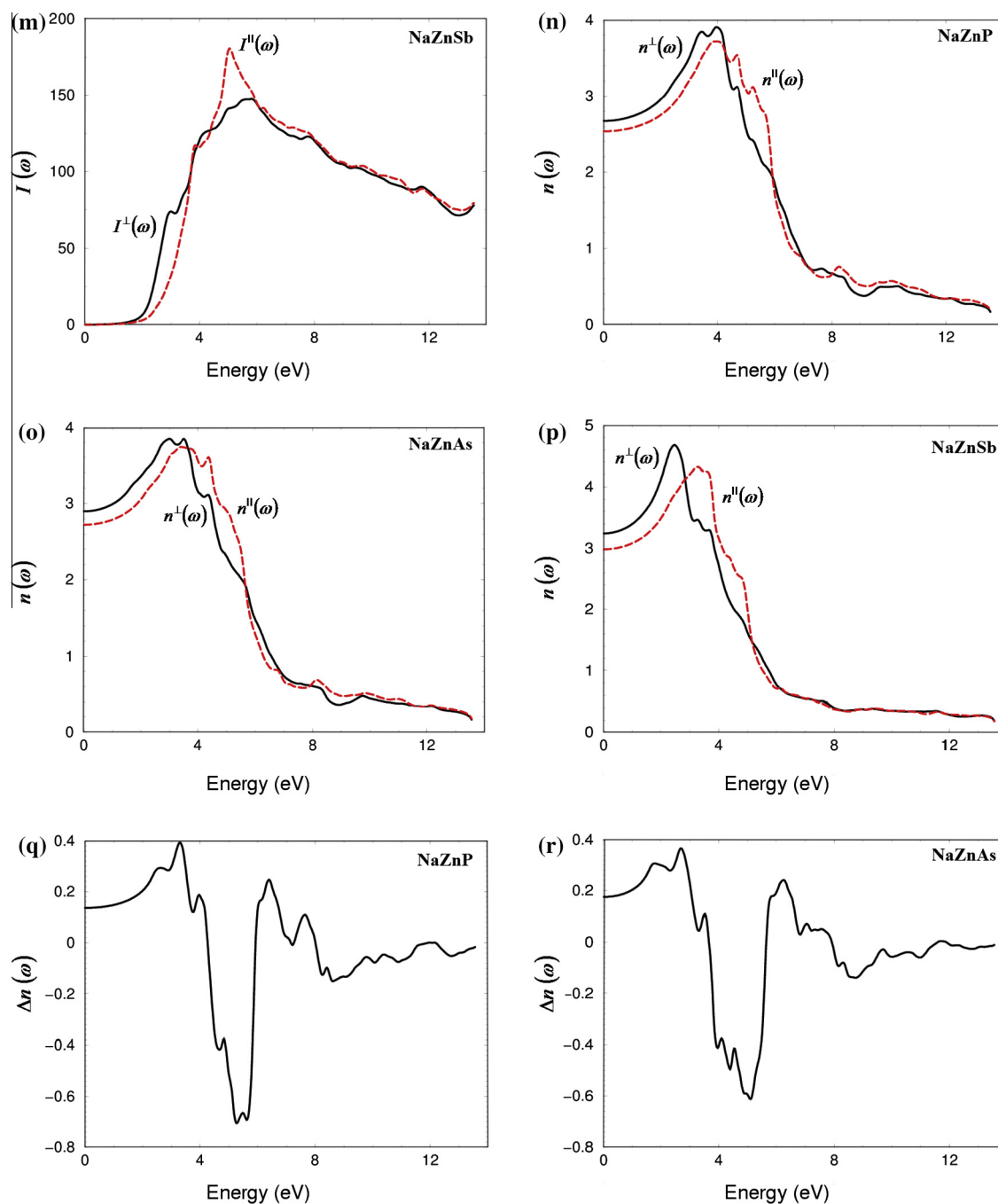


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presented one main peak for each of $\varepsilon_2^{\parallel}(\omega)$ and $\varepsilon_2^{\perp}(\omega)$. The positions of these peaks are 4.5 eV ($\varepsilon_2^{\perp}(\omega)$), 5.0 eV ($\varepsilon_2^{\parallel}(\omega)$) for NaZnP, 4.0 eV ($\varepsilon_2^{\perp}(\omega)$) and 4.5 eV ($\varepsilon_2^{\parallel}(\omega)$) for NaZnAs, and 3.0 eV ($\varepsilon_2^{\perp}(\omega)$) and 3.5 eV ($\varepsilon_2^{\parallel}(\omega)$) for NaZnSb. The origin of these peaks is due to the inter-band transitions from the occupied Na-s/p, Zn-s/p/d and P/As/Sb-s/p/d states to the unoccupied Na-s/p, Zn-s/p/d and P/As/Sb-s/p/d states. We should emphasize that there exists a considerable anisotropy between $\varepsilon_2^{\parallel}(\omega)$ and $\varepsilon_2^{\perp}(\omega)$ components.

To identify the origin of the peaks in the optical spectra of Nowotny–Juza NaZnX (X = P, As and Sb) compounds we considered the optical transition matrix elements. To demonstrate the optical transitions which determined by the electric-dipole transitions between the occupied and the unoccupied bands, we have used the band structures diagrams of NaZnP, NaZnAs and NaZnSb to clearly show the optical transitions depicted on a generic band structure, as prototype we show in Fig. 3(d) the optical transitions in NaZnP compound. The allowed optical transitions are labeled according to the spectral peak positions in $\varepsilon_2(\omega)$

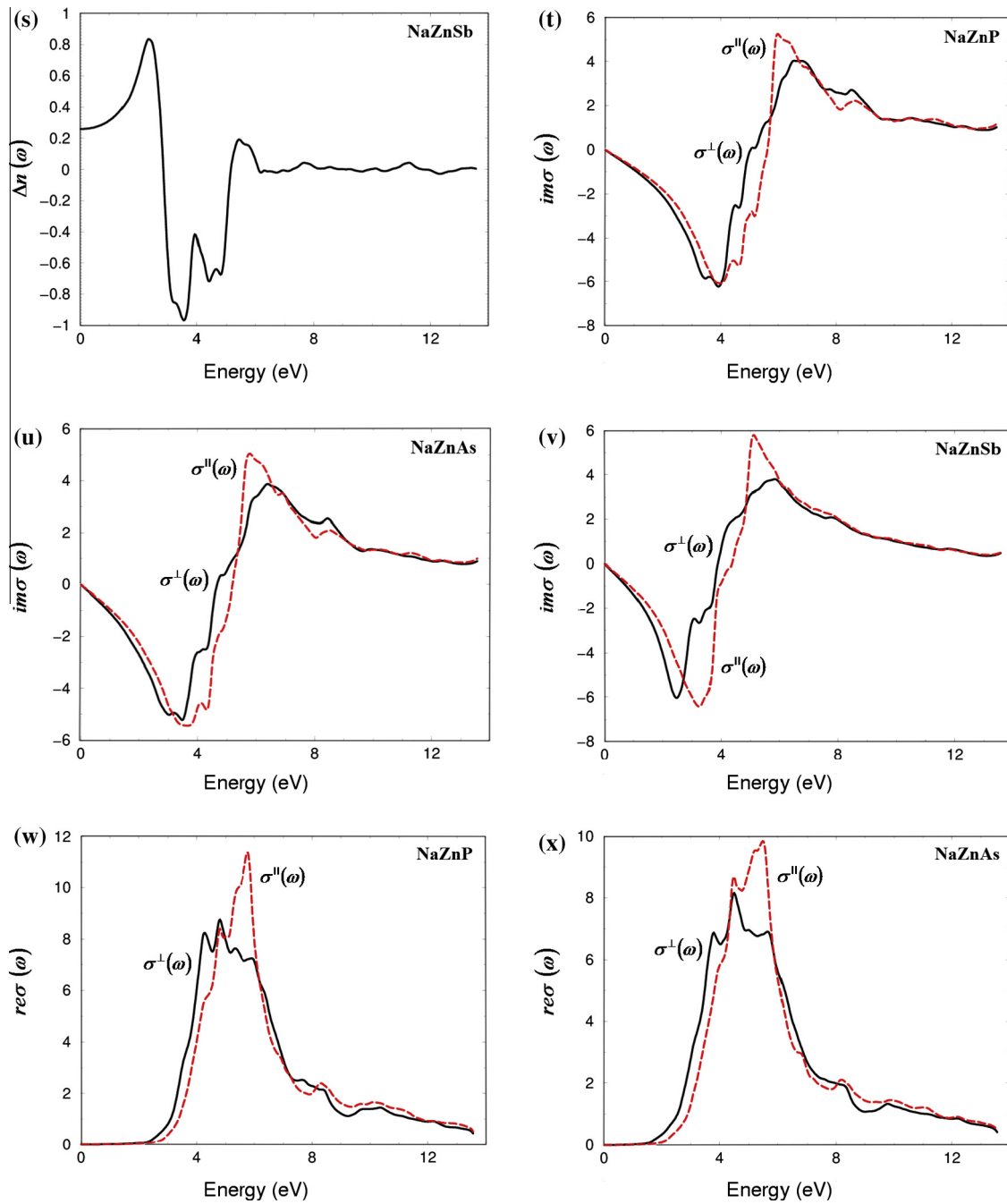


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(Fig. 3(a–c)). For simplicity we have labeled the transitions in Fig. 3(a) and (d), as A, B, and C. The transitions (A) are responsible for the structures for $\varepsilon_2(\omega)$ in the spectral range 0.0–5.0 eV; the transitions (B) 5.0–10.0 eV, and the transitions (C) 10.0–14.0 eV. From the imaginary part of the optical dielectric function the real part can be obtained using the Kramers–Kronig relations (Wooten, 1972).

Fig. 3(e–g) show $\varepsilon_1^{\parallel}(\omega)$ and $\varepsilon_1^{\perp}(\omega)$ of Nowotny–Juza NaZnX (X = P, As and Sb) compounds, again it show a considerable anisotropy between the two components. We have listed the values of $\varepsilon_1^{\parallel}(0)$ and $\varepsilon_1^{\perp}(0)$ in Table 1, which show that a smaller energy gap yields a larger $\varepsilon_1(0)$ value. This

could be explained on the basis of the Penn model (1962). Penn proposed a relation between $\varepsilon(0)$ and E_g , $\varepsilon(0) \approx 1 + (\hbar\omega_P/E_g)^2$. E_g is some kind of averaged energy gap which could be related to the real energy gap. It is clear that ε is inversely proportional with E_g . Hence a larger E_g yields a smaller $\varepsilon(0)$. From the calculated values of $\varepsilon_1^{\parallel}(0)$, $\varepsilon_1^{\perp}(0)$ and $\varepsilon_1^{tot}(0)$ one can obtain the uniaxial anisotropy $\delta\varepsilon = [(\varepsilon_0^{\parallel} - \varepsilon_0^{\perp})/\varepsilon_0^{tot}]$. The $\delta\varepsilon$ values are listed in Table 1, which indicate the existence of the considerable anisotropy.

Since the optical properties give deep insight into the electronic structure, therefore we have calculated the other

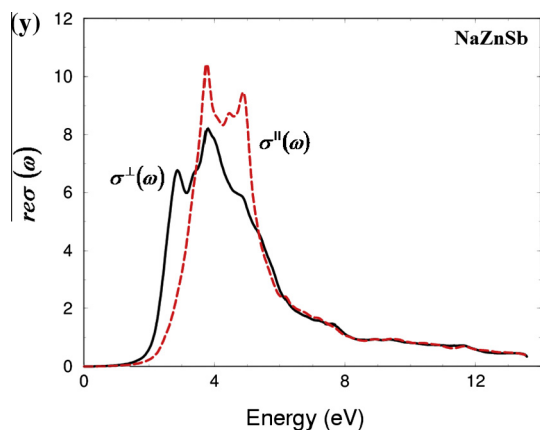


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related optical response for instance $R(\omega)$, $I(\omega)$, $n(\omega)$, $\Delta n(\omega)$, $im\sigma(\omega)$ and $re\sigma(\omega)$. The reflectivity spectra $R^{\parallel}(\omega)$ and $R^{\perp}(\omega)$ are depicted in Fig. 3(h–j). It is clear that at low energies between 0.0 and 2.5 eV the optical reflectivity of the three compounds starts between 18.0% and 28.0%. Then after the reflectivity spectra increases rapidly to form the first reflectivity maximum of about 62.0%, 65.0% and 68.0% which are occurs between 6.0–10.0 eV, 5.0–10.0 eV and 4.0–9.0 eV for NaZnX (X = P, As and Sb) compounds, respectively. The first reflectivity maximum formed by transition of s/p-states of VB to s/p/d-states of CB. There exists an abrupt reduction in the reflectivity spectrum at energies between 10.0 and 12.0 eV which confirm the occurrence of a collective plasmon resonance. The depth of the plasmon minimum is determined by the imaginary part of the dielectric function at the plasma resonance and is representative of the degree of overlap between the inter-band absorption regions. The values of R^{\parallel} and R^{\perp} are listed in Table 1. The optical absorption coefficient of the investigated compounds as represented in Fig. 3(k–m) exhibit that the optical absorption edges occurs at 1.80, 1.47 and 0.25 eV, then after the absorption coefficient increases drastically to reach its maximum value at around 5.0 eV. We should emphasize that the Nowotny–Juza NaZnX (X = P, As and Sb) compounds have wide optical transparency region extended between 88.5 nm up to 4960 nm. The refractive indices $n^{\parallel}(\omega)$ and $n^{\perp}(\omega)$ of the investigated compounds as depicted in Fig. 3(n–p) are confirm the existence of the considerable anisotropy. With the aid of the refractive indices one can obtain the birefringence as illustrated in Fig. 3(q–s). The birefringence $\Delta n(\omega)$ is defined as a difference between the extraordinary and ordinary refraction indices, $\Delta n(\omega) = n_e(\omega) - n_o(\omega)$, where $n_o(\omega)$ is the index of refraction for an electric field oriented along the c -axis (ordinary index of refraction) and $n_e(\omega)$ is the index of refraction for an electric field perpendicular to the c -axis (extraordinary index of refraction). The value of the birefringence $\Delta n(0)$ and the corresponding refractive indices $n^{\parallel}(0)$ and $n^{\perp}(0)$ at the static limit are given in Table 1. The calculated imaginary $im\sigma^{\parallel}(\omega)$ and

$im\sigma^{\perp}(\omega)$ and real $re\sigma^{\parallel}(\omega)$ and $re\sigma^{\perp}(\omega)$ parts of the optical conductivity are shown in Fig. 3(t–y). The optical conductivity is directly proportional to the frequency-dependent dielectric function $\varepsilon(\omega)$ through $\varepsilon(\omega) = 1 + \frac{4\pi i\sigma(\omega)}{\omega}$. Both of $im\sigma^{\parallel}(\omega)$ and $im\sigma^{\perp}(\omega)$ exhibit a negative values with deep valley between 0.0 and 5.0 eV, then after they exhibit appositve peaks around 7.0 eV. Whereas $re\sigma^{\parallel}(\omega)$ and $re\sigma^{\perp}(\omega)$ exhibit a spectral structure similar to that of $\varepsilon_1^{\parallel}(\omega)$ and $\varepsilon_1^{\perp}(\omega)$.

4. Conclusions

We have employed the FPLAPW method as embodied in the WIEN2k code, within the recently modified Becke–Johnson potential (mBJ) to calculate the electronic band structure, total and partial density of states and the optical properties of Nowotny–Juza NaZnX (X = P, As and Sb) compounds at ambient pressure. Calculation shows that these compounds are narrow direct band gap semiconductors. Substituting P by As cause to push the CB’s toward Fermi level by around 0.33 eV, while substituting As by Sb led to dramatic changes in the locations and the bandwidths of the CB’s, resulting in huge reduction in the band gap of about 1.55 eV with respect to NaZnP. The band gap reduction is attributed to the fact that the atomic radius of Sb > As > P, therefore the small difference between P and As radius led to small shifts in the CB’s toward E_F , whereas the big difference between P and Sb radius is the reason behind the huge reduction in the NaZnSb band gap with respect to NaZnAs and NaZnP. We should emphasize that since the electro-negativity difference between P, As and Sb is very small therefore substituting P → As → Sb will not introduce more peaks in the DOS above the CBM. The optical properties confirm the band gap’s reduction and gave deep insight into the electronic structure by showing the existence of the considerable anisotropy and the original of the spectral peak structures through the optical transitions between the occupied and unoccupied bands.

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References

- Baciewicz, R., Cizek, T.F., 1988. Preparation and characterization of some $A^I B^{II} C^V$ type semiconductors. *Appl. Phys. Lett.* 52, 1150.

- Beleanu, A., Mondeshki, M., Juan, Q., Casper, F., Felser, C., Porcher, F., 2011. Systematical, experimental investigations on LiMgZ (Z = P, As, Sb) wide band gap semiconductors. *J. Phys. D Appl. Phys.* 44, 475302.
- Blaha, P., Schwarz, K., Madsen, G.K.H., Kvasnicka, D., Luitz, J., 2001. WIEN2K, “An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties”, Karlheinz Schwarz. Techn. Universitat, Wien, Austria, ISBN 3-9501031-1-2.
- Carlsson, A.E., Zunger, A., Wood, D.M., 1985. Electronic structure of LiZnN: interstitial insertion rule. *Phys. Rev. B* 32, 1386.
- Charifi, Z., Baaziz, H., Noui, S., Ugur, S., Ugur, G., Iyigor, A., Candan, A., Al-Douri, Y., 2014. Phase transition of Nowotny–Juza NaZnX (X = P, As and Sb) compounds at high pressure: theoretical investigation of structural, electronic and vibrational properties. *Comput. Mater. Sci.* 87, 187.
- Davis, R., Knight, J.R., 1975. Operation of GaAs solar cells at high solar flux density. *Sol. Energy* 17, 145.
- Deshmukh, M.P., Nagaraju, J., 2005. Measurement of silicon and GaAs/Ge solar cells ac parameters. *Sol. Energy* 78, 1.
- Gao, S., 2003. Linear-scaling parallelization of the WIEN package with MPI. *Comput. Phys. Commun.* 153, 190.
- Hufner, S., Claessen, R., Reinert, F., Straub, Th., Strocov, V.N., Steiner, P., 1999. Photoemission spectroscopy in metals: band structure-Fermi surface–spectral function. *J. Electron Spectra. Relat. Phenom.* 100, 191.
- Jaiganesh, G., Merita, T., 2008. Electronic and structural properties of NaZnX (X = P, As, Sb): an ab initio study. *J. Phys.: Condens. Matter* 20, 085220.
- Kumar, R.A., Suresh, M.S., Nagaraju, J., 2004. GaAs/Ge solar cell AC parameters under illumination. *Sol. Energy* 76, 417.
- Kuriyama, K., Kato, T., Kawada, K., 1994a. Optical band gap of the filled tetrahedral semiconductor LiZnAs. *Phys. Rev. B* 49, 11452.
- Kuriyama, K., Kato, T., Tanaka, T., 1994b. Optical band gap of the filled tetrahedral semiconductor LiZnN. *Phys. Rev. B* 49, 4511.
- Lee, Joo.-Hyoung., Junqiao, Wu., Grossman, Jeffrey C., 2010. Enhancing the thermoelectric power factor with highly mismatched isoelectronic doping. *Phys. Rev. Lett.* 104, 016602.
- Madsen, G.K.H., 2006. Automated search for new thermoelectric materials: the case of LiZnSb. *J. Am. Chem. Soc.* 128, 12140.
- Minwoo, Nam, Kangho, Kim, Jaejin, Lee, Kee-Keun, Lee, Sang Sik, Yang, 2013. Concentrating microlens array mounted on an InGaP/GaAs/Ge solar cell for photovoltaic performance enhancement. *Sol. Energy* 91, 374.
- Penn, D.R., 1962. Wave-number-dependent dielectric function of semiconductors. *Phys. Rev. B* 128, 2093.
- Reshak, A.H., Kamarudin, H., Auluck, S., 2013a. Dispersion of the linear and nonlinear optical susceptibilities of disilver germanium sulfide from DFT calculations. *J. Mater. Sci.* 48, 1955.
- Reshak, A.H., Charifi, Z., Baaziz, H., 2013b. The influence of the lattice relaxation on the optical properties of Ga_{N_x}As_{1-x} alloys. *Sol. Energy* 90, 134.
- Schwarz, K., 2003. DFT calculations of solids with LAPW and WIEN2k. *J. Solid State Chem.* 176, 319.
- Tran, F., Blaha, P., 2009. Accurate band gaps of semiconductors and insulators with a semilocal exchange-correlation potential. *Phys. Rev. Lett.* 102, 226401.
- Ul Haq, B., Ahmed, R., El Haj Hassan, F., Khenata, R., Khalid Kasmin, M., Goumri-Said, S., 2014. Mutual alloying of XAs (X = Ga, In, Al) materials: tuning the optoelectronic and thermodynamic properties for solar energy applications. *Sol. Energy* 100, 1.
- Wei, Su.-Huai., Zunger, A., 1986. Electronic structure and phase stability of LiZnAs: a half ionic and half covalent tetrahedral semiconductor. *Phys. Rev. Lett.* 56, 528.
- Wood, D.M., Zunger, A., de Groot, R., 1985. Electronic structure of filled tetrahedral semiconductors. *Phys. Rev. B* 31, 2570.
- Wooten, F., 1972. *Optical Properties of Solids*. Academic Press, New York and London.