

The Quasiparticle Electronic Structure of Trigonal CaSnO_3 and ZnSnO_3 Crystals

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The electronic structure of trigonal CaSnO_3 and ZnSnO_3 crystals was obtained taking into account the quasiparticle corrections to the electron energies, found by means of the Green's function. At the *first stage*, optimization of the atomic coordinates was realized with the minimization of the total-energy functional and components of the stress tensor. The obtained values of the structural parameters of all crystals have shown a good comparison with the results found by other authors. The *second stage* was devoted to the calculation of the energy eigenvalues and wave functions within the GGA approach. These results were used in the *third stage* for calculation of the Green's function. The GGA-GW scheme of finding the Green's function, based on the obtained GGA one-particle states, was applied to all crystals. It is established that the fundamental band gaps E_g , calculated within the GGA and GW approaches, are indirect in ilmenite-type CaSnO_3 (Γ - Γ') and ZnSnO_3 (Γ - Γ_L). All band gaps found by means of the GGA approach are significantly smaller than the corresponding values obtained within the GW approximation. In particular, in ilmenite-type CaSnO_3 the indirect gaps are $E_g^{GGA} = 2.92$ eV and $E_g^{GW} = 4.54$ eV. In ilmenite-type ZnSnO_3 , they are $E_g^{GGA} = 1.47$ eV and $E_g^{GW} = 3.69$ eV. In ZnSnO_3 with the LiNbO_3 type structure, the calculated direct gaps are (Γ - Γ) $E_g^{GGA} = 1.20$ eV and $E_g^{GW} = 3.57$ eV. The values of the band gaps obtained within the quasiparticle GW approximation are well compared with the experiment. A systematic investigation of the band gap dependence on starting approximation to the GW was carried out in case of trigonal CaSnO_3 . GW calculations based on HSE06 reveal that the amount of exact Hartree-Fock exchange (mixing parameter) of 0.28 leads to reproducing the experimental band gap of ilmenite-type CaSnO_3 . The quasiparticle energy bands in ilmenite-type CaSnO_3 and ZnSnO_3 have been found here for the first time.

Keywords: Electronic structure, Green's function, GW, Quasiparticles.

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1. INTRODUCTION

Interest in alkaline earth stannates has recently increased due to the wide range of applications. Calcium stannate, CaSnO_3 , is known as a promising capacitor component, high-capacity anode in Li-ion batteries and phosphorescent material [1], while ZnSnO_3 compound is a potential ferroelectric material with significant polarization. High polarization of $59 \mu\text{C}/\text{cm}^2$ has been reported in synthesized ZnSnO_3 samples under a pressure of 7 GPa [2].

CaSnO_3 exists in a few crystalline forms including orthorhombic GdFeO_3 -type perovskite structure and rhombohedral ilmenite phase. The ilmenite variety of CaSnO_3 is a metastable phase and can be transformed into the perovskite structure by annealing at 900°C [3]. ZnSnO_3 was synthesized both in a rhombohedral LiNbO_3 -type and ilmenite-type structure by a solid-state reaction under high pressure and ion-exchange reaction, respectively [2, 4].

Orthorhombic CaSnO_3 and ZnSnO_3 with LiNbO_3 -type (LN) structure are more studied both experimentally and theoretically. But a little attention has been paid to the ilmenite variety of these compounds. An important focus is the understanding of the role of electronic structure in determining interesting properties and realizing promising applications.

In ilmenite-type (IL) CaSnO_3 and ZnSnO_3 , the values of band gaps of 4.4 eV and 3.7 eV were obtained from the optical absorption spectra [5]. The electronic structure of IL-type CaSnO_3 was studied from the first principles only by Mizoguchi et al., but a brief discussion was made on this type compound [5]. Also there are only a few ab initio

calculations of the electronic structure of IL-type ZnSnO_3 within the generalized gradient approximation (GGA) and PBE0 hybrid functional [6-8]. But the GGA does not allow to treat correctly the band gaps and significantly underestimates them [6, 7]. The band gap value, calculated by means of the PBE0 approach, is much closer to the experimental data than the GGA one [8].

In this work, we have performed the electronic structure calculations of trigonal CaSnO_3 and ZnSnO_3 crystals within the GW method [9] based on many-body perturbation theory. In the GW approximation, the quasiparticle corrections to the eigenenergies were obtained in terms of the screened Coulomb exchange interaction and Green's functions calculated on the top of the GGA or hybrid functional results. The GW approach enables to reproduce accurately the band structure of insulators. This method has been used quite successfully for predicting the electronic structure and especially the band gaps of $(\text{Ba}, \text{Sr})\text{SnO}_3$ [10]. The main disadvantage is that the GW approximation is quite expensive and computational cost increases significantly with the system size.

2. CALCULATION DETAILS

At the first stage, the Kohn-Sham equation is solved self-consistently with the exchange-correlation potential defined in terms of the GGA or HSE06 approximations [11]:

$$(-\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}))\varphi_{nk}(\mathbf{r}) = \varepsilon_{nk}\varphi_{nk}(\mathbf{r}),$$

where ∇^2 is the kinetic energy operator; V_{ext} , V_H and

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V_{xc} are the external, Hartree and exchange-correlation potentials, respectively; \mathbf{k} denotes the wave vector in the 1st Brillouin zone and n is the band index.

At the second stage, the quasiparticle energies and eigenfunctions are determined from the quasiparticle equation [20]:

$$(-\nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}))\psi_{n\mathbf{k}}(\mathbf{r}) + \int \Sigma(\mathbf{r}, \mathbf{r}', E_{n\mathbf{k}})\psi_{n\mathbf{k}}(\mathbf{r}')d\mathbf{r}' = E_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r}),$$

where Σ is the nonlocal self-energy operator.

The quasiparticle wave functions are expressed in terms of the basis Kohn-Sham eigenstates, evaluated at the first stage with the GGA or HSE06 exchange-correlation functional, as follows:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \Sigma a_{nn} \varphi_{n\mathbf{k}}(\mathbf{r}).$$

Correspondingly, the quasiparticle perturbative Hamiltonian can be found by

$$H_{nn}(E) = \varepsilon_{nk} \delta_{nn'} + \langle \varphi_{n\mathbf{k}} | \Sigma(E) - V_{xc} | \varphi_{n\mathbf{k}} \rangle,$$

where difference $\Sigma(E) - V_{xc}$ represents the perturbation.

The HSE exchange-correlation energy functional is defined as [12]

$$E_{xc}^{HSE} = \alpha E_x^{HF,short}(\omega) + (1-\alpha)E_x^{PBE,short}(\omega) + E_x^{PBE,long}(\omega) + E_c^{PBE},$$

where E_x^{HF} and E_x^{PBE} are the Hartree-Fock and PBE exchange energies, respectively, and E_c^{PBE} is the PBE correlation energy. The parameter α mixes the exact E_x^{HF} exchange, depending on wave functions, with the GGA exchange E_x^{PBE} , depending on electron density. The adjustable parameter ω defines the range, in which the fast-decaying Coulomb SR term tends to zero. The slowly decaying long-range part of the Hartree-Fock exchange is replaced by long-range limit of E_x^{PBE} exchange. The range-separation parameter ω was set according to the HSE06 hybrid exchange-correlation functional [12]. We have used different mixing parameters in the range $0 \leq \alpha \leq 0.5$ for electronic structure calculations of trigonal CaSnO_3 . Finally, its value of 0.28 was chosen as the best in the tuning of the band gap in trigonal CaSnO_3 crystal.

All calculations were performed using the ABINIT software package [13]. The energy cutoff of 870 eV was chosen for the setting of the plane wave basis. We have applied $4 \times 4 \times 4$ Monkhorst-Pack grid [14] for 30-atoms unit cell of trigonal CaSnO_3 and ZnSnO_3 crystals in the GW band structure calculations. Total and partial densities of states (DOS) were obtained within the GGA on $6 \times 6 \times 6$ Monkhorst-Pack grid. We have used the projector augmented waves (PAW) [15] as a single-particle basis states. The PAW basis functions and pseudopotentials were generated by means of the AtomPAW code [15] for the following valence configurations: $\{3d^{10}4s^2\}$ for Zn, $\{4d^{10}5s^25p^2\}$ for Sn, and $\{2s^22p^4\}$ for O atom, respectively. The corresponding radii of the augmentation spheres are equal to 1.9, 2.38, and 1.41 a.u., respectively. The electronic structure of IL-type CaSnO_3 was calculated

using the norm-conserving pseudopotentials.

We have performed the structural relaxation of trigonal CaSnO_3 , ZnSnO_3 . All the stress tensor components were less than 0.02 GPa. The calculated lattice constants of the relaxed unit cell and experimental data are listed in Table 1. Obtained structural parameters within the GGA are in good agreement with other theoretical findings [6-8].

Table 1 – Calculated lattice constants a (Å), c (Å) and volume V (Å³/formula unit) of trigonal CaSnO_3 , ZnSnO_3 in comparison with experimental data

	Space group	a	c	V	
IL-type CaSnO_3	R-3	5.487	15.287	66.45	Expt.[3]
		5.569	15.463	69.22	Calc.
IL-type ZnSnO_3	R-3	5.284	14.091	56.78	Expt.[4]
		5.373	14.316	59.65	Calc.
LN-type ZnSnO_3	R3c	5.262	14.003	55.97	Expt.[2]
		5.348	14.213	58.67	Calc.

3. RESULTS AND DISCUSSION

As it was mentioned above, GGA approximation is the starting point in the GW method. According to our GGA calculations, an indirect band gap of 1.47 eV is found in IL-type ZnSnO_3 : the maximum of the valence band occurs between Γ and L points, while the minimum of the conduction band is at Γ point. The calculated band gap value is still dramatically underestimated compared to the experimental data of 3.7 eV. By further applying the GW method based on GGA eigenvalues, the same location of the top of the valence band is eventually obtained. The band gap increased to 3.69 eV which is very close to the experimental data. The electronic structure of IL-type ZnSnO_3 calculated by means of the GW method is shown in Fig. 1.

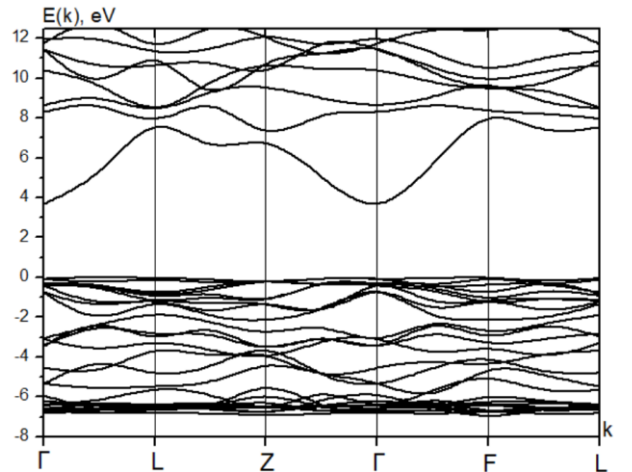


Fig. 1 – The electronic structure of ilmenite-type ZnSnO_3 obtained within the GW method based on GGA

Unlike the IL-type ZnSnO_3 crystal, the LN-type ZnSnO_3 has a direct Γ - Γ band gap found both within the GGA and GW approaches. The band gap value, calculated within the GGA, equals to 1.20 eV and is underestimated.

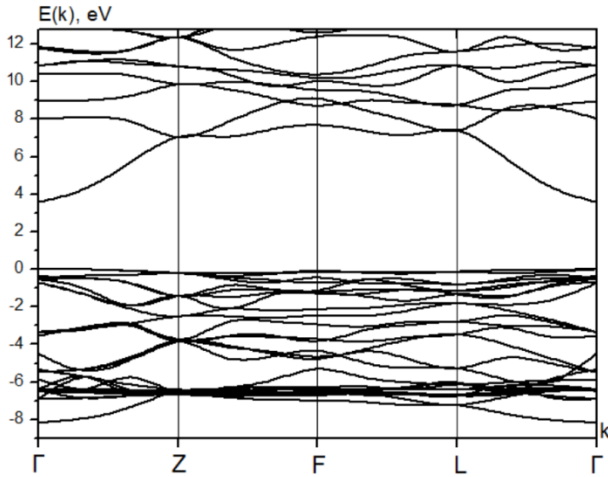


Fig. 2 – The electronic structure of LiNbO₃-type ZnSnO₃ obtained within the GW method based on GGA

The electronic structure of LN-type ZnSnO₃ calculated by means of the GW method is shown in Fig. 2. The calculated band gap value of 3.57 eV is compared well with experimental determinations ranging from 3.3 to 3.9 eV [16, 17].

Table 2 – Calculated direct and indirect band gaps (in eV) of ZnSnO₃

ilmeneite-type ZnSnO ₃			
	E_{GGA}	E_{GW}	$E_{GW}-E_{GGA}$
Γ - Γ L	1.47	3.69	2.22
Γ - Γ	1.54	3.78	2.24
L-L	4.69	7.58	2.89
Z-Z	4.23	6.94	2.71
F-F	5.00	7.98	2.98
LiNbO ₃ -type ZnSnO ₃			
	E_{GGA}	E_{GW}	$E_{GW}-E_{GGA}$
Γ - Γ	1.20	3.57	2.37
L-L	4.56	7.53	2.97
Z-Z	4.47	7.25	2.78
F-F	4.59	7.77	3.18

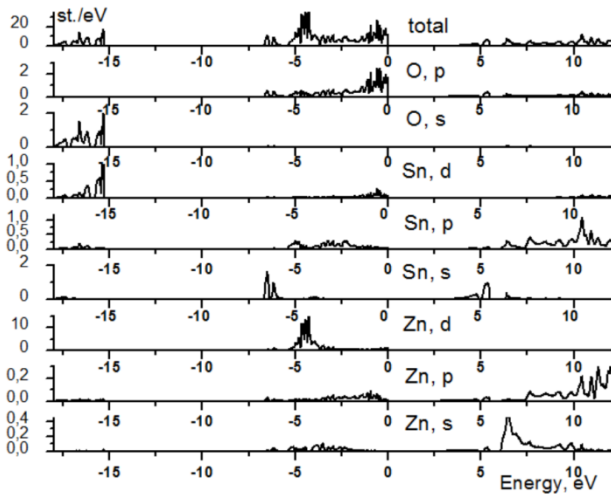


Fig. 3 – The partial and total densities of states of ilmeneite-type ZnSnO₃ obtained within the GGA

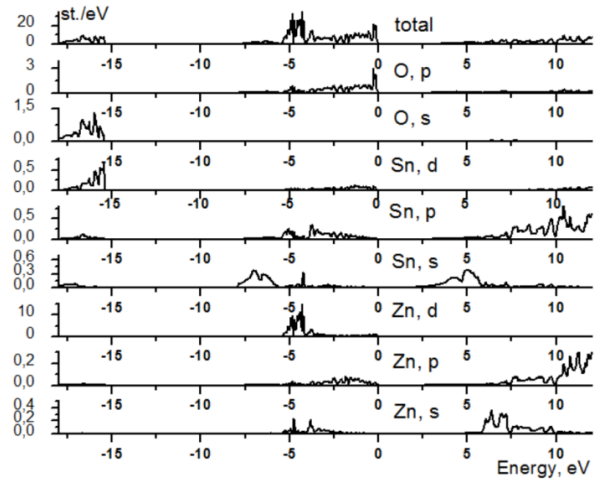


Fig. 4 – The partial and total DOS of LiNbO₃-type ZnSnO₃ obtained within the GGA

Table 2 summarizes the indirect and direct gaps of IL- and LN-type ZnSnO₃ obtained in this work within the GGA and GW approaches. As can be seen, the differences between GW and GGA gaps ($\Delta = E_{GW} - E_{GGA}$) are not constant. The GW approach leads to significant gap opening, while the GGA values of the indirect or direct band gaps show a significant underestimation.

Fig. 3 and Fig. 4 represent the total and partial DOS of the ZnSnO₃ computed within the GGA. In both IL- and LN-type ZnSnO₃ crystals, the upper part of the valence band is mainly composed of the Zn and Sn *p* and *d*, and O *p* states, respectively. The bottom of the conduction band is derived from Sn *s* states. Compared to LN-type ZnSnO₃, the partial DOS of IL-type have slightly different peak positions. The valence band becomes less extended. The lowest conduction band states are shifted toward higher energies.

In a recent work it was shown that the G_0W_0 approximation improves the value of the band gap in LN-type ZnSnO₃, which equals to 3.0 eV [19]. We note that the band gap value of the LN-type ZnSnO₃, calculated here within the GW, differs from those obtained in the work [19], where in the G_0W_0 approach, the PBEsol eigenvalues were used as a starting point. The IL-type ZnSnO₃ is less studied compared to LN-type. Recent calculations of the electronic structure of the IL-type ZnSnO₃ were performed within the GGA approach [7]. The location of the valence band maximum is still a matter of debate. In work [6], an indirect band gap of 1.4 eV was found in the IL-type ZnSnO₃ within the pseudopotential plane wave approach, the top of the valence band is located between K and Γ points, and the bottom of the conduction band appears at Γ point. Another GGA study predicts the valence band maximum between Γ and X points [7]. Our GGA and GW calculations agree well with earlier results on the indirect gap in the IL-type ZnSnO₃. On the other hand, in work [8], the direct Γ - Γ gaps of 1.063 eV and 3.977 eV were obtained by means of the GGA-PW91 and PBE0 approaches, respectively. According to our GW study, the direct Γ - Γ gap is higher by 0.09 eV than the indirect band gap in the IL-type ZnSnO₃ as shown in Table 2. The difference between our and PBE0 based results can be explained by the fact that different basis was used in the calculations.

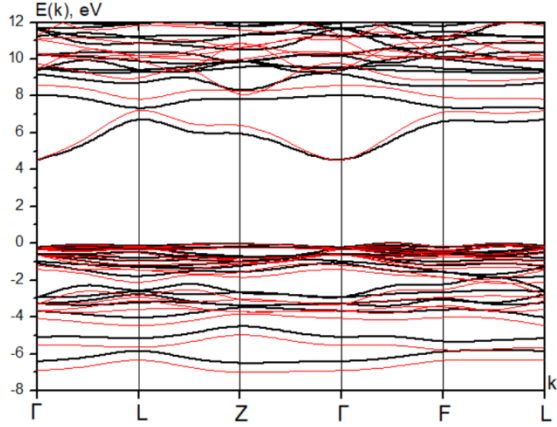


Fig. 5 – The electronic structure of ilmenite-type CaSnO_3 obtained within the GW method based on GGA (red line) and the GW based on HSE06 (black line) approaches

As can be expected, GGA underestimates the band gap in case of the IL-type CaSnO_3 ; we have found the indirect gap value of 2.92 eV. We also have calculated the electronic structure of trigonal CaSnO_3 within the GW method based on the GGA eigenvalues. Our calculations showed that the IL-type CaSnO_3 is an indirect band gap material with the gap value of 4.54 eV. Experimentally the band gap of trigonal CaSnO_3 was found to be 4.4 eV [5]. In this case, the standard GGA-based GW slightly overestimates the gap value. For comparison, the GW approach, based on HSE06 eigenvalues, was chosen to calculate the electronic structure of the IL-type CaSnO_3 . We have noticed that the band gap value clearly depends on the mixing parameter a . According to our calculations, the value $a = 0.28$ led to the best agreement with the experimental measurements. So a is the system dependent parameter as has been reported previously [18]. Therefore the indirect gap is diminished to 4.39 eV. Fig. 5 illustrates the calculated electronic structure of trigonal CaSnO_3 by means of the GW method, starting from GGA and HSE06, respectively.

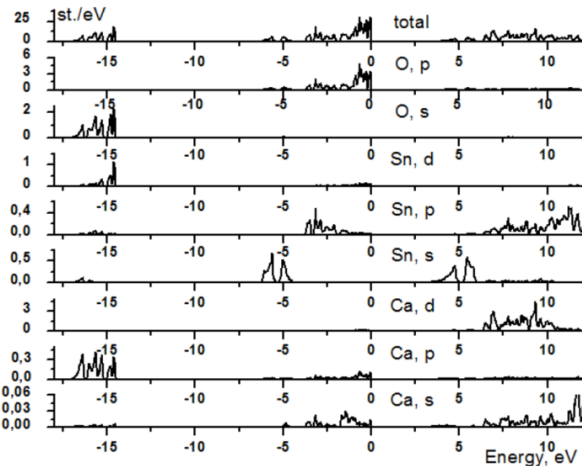


Fig. 6 – The partial and total DOS of ilmenite-type CaSnO_3 obtained within the GGA

Both GGA and HSE06-based GW approaches predict the valence band maximum between Γ and F points in the IL-type CaSnO_3 . The conduction band minimum occurs at Γ point. The top of the valence band originates

generally from the O p , Ca p and Sn p and d states, as can be seen from the partial DOS plotted in Fig. 6. The bottom of the conduction band is formed predominantly by the Sn s states.

The results for the band gaps found in trigonal CaSnO_3 within different approximations are shown in Table 3. The band gap value of the IL-type CaSnO_3 found in the HSE06-based GW approach is well compared to the experimental data.

Table 3 – Calculated direct and indirect band gaps (in eV) of ilmenite-type CaSnO_3 . *GW I* and *GW II* denote GW method based on GGA and HSE06, respectively

ilmenite-type CaSnO_3					
	E_{GGA}	E_{GWI}	$E_{GWI-E_{GGA}}$	E_{GWII}	$E_{GWI-E_{GWII}}$
Γ - Γ F	2.92	4.54	1.62	4.39	0.15
Γ - Γ	3.17	4.77	1.60	4.75	0.02
L-L	4.94	7.41	2.47	6.86	0.55
Z-Z	4.27	6.44	2.17	6.00	0.44
F-F	4.88	7.28	2.40	6.80	0.48

Earlier the electronic structure of binary and ternary oxides containing Sn^{4+} , Sb^{5+} and Bi^{5+} was calculated by means of the linear muffin-tin orbital (LMTO) method with the Perdew-Wang GGA exchange-correlation functional [5]. The band gap of 4.0 eV was obtained for the ilmenite variety of CaSnO_3 , but the band structure of this compound was not discussed in detail. The band energies, evaluated here within the GGA-based GW approach in the IL-, LN-type ZnSnO_3 , as well as within the HSE06-based GW in trigonal CaSnO_3 , are close to the available experimental data.

4. CONCLUSIONS

In this work, we have employed the many-body perturbation theory in the GW approximation to electronic structure calculations of trigonal CaSnO_3 and ZnSnO_3 crystals. First, we have calculated the electronic band energies by means of the GGA, the band gaps were considerably underestimated by about 34-64 %. Then the quasiparticle corrections to the eigenenergies were evaluated within the single-particle Green's function calculated on the level of the GGA or HSE06 results. The differences between the calculated direct or indirect gaps within the GGA and GW methods were also examined.

As pointed out previously, GW starting from GGA reaches the measured values of the band gaps in IL- and LN-type ZnSnO_3 . We have found a weak band gap dependence on starting approximation to GW in case of IL-type CaSnO_3 . The GGA-GW approach makes the band gap prediction slightly less accurate for CaSnO_3 . The small overestimation of the band gap value can be improved by using the HSE06-GW approach. Using the exchange-correlation functional HSE06, with optimized mixing parameter, as a starting point for the GW approximation, results in a tuning the band gap value of IL-type CaSnO_3 to the experimental data. Our calculations show that the HSE06-GW approach with optimal mixing parameter of 0.28 is the most appropriate for treating the band structure in trigonal CaSnO_3 . The quasiparticle electronic structure of ilmenite variety of CaSnO_3 and ZnSnO_3 crystals, presented here for the first time, will be useful for further investigation of these compounds.

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Квазічастинкова електронна структура тригональних кристалів CaSnO_3 та ZnSnO_3

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Електронна структура тригональних кристалів CaSnO_3 та ZnSnO_3 була отримана з урахуванням квазічастинкових поправок до власних енергій електронів, знайдених за допомогою функції Гріна. На першому етапі оптимізація атомних координат була реалізована мінімізацією функціонала повної енергії та складових тензора напружень. Отримані значення структурних параметрів усіх кристалів виявили добре зіставлення з результатами, знайденими іншими авторами. Другий етап був присвячений розрахунку власних значень енергії та хвильових функцій у підході GGA. Ці результати були використані на третьому етапі для розрахунку функції Гріна. Схема GGA-GW знаходження функції Гріна на основі отриманих одночастинкових станів підходу GGA була застосована для усіх кристалів. Встановлено, що отримані у підходах GGA та GW фундаментальні міжзонні щілини E_g є непрямыми в ільменітах CaSnO_3 (Γ - Γ F) та ZnSnO_3 (Γ - Γ L). Всі міжзонні щілини, знайдені у підході GGA, є суттєво меншими відповідних значень, отриманих у наближенні GW. Зокрема, у ільменіті CaSnO_3 непряма щілина $E_g^{GGA} = 2.92$ eV, а $E_g^{GW} = 4.54$ eV. У ільменіті ZnSnO_3 непряма щілина $E_g^{GGA} = 1.47$ eV, а $E_g^{GW} = 3.69$ eV. У кристалі ZnSnO_3 зі структурою типу LiNbO_3 обчислена пряма щілина (Γ - Γ) $E_g^{GGA} = 1.20$ eV, а $E_g^{GW} = 3.57$ eV. Значення міжзонних щілин, отриманих у квазічастинковому наближенні GW, добре зіставляються з експериментом. Систематичне дослідження залежності ширини забороненої зони від початкового наближення до GW було виконано у тригональному кристалі CaSnO_3 . Розрахунки GW на основі HSE06 показують, що величина точного обміну Хартрі-Фока (параметр змішування) 0.28 приводить до відтворення експериментальної щілини ільменіту CaSnO_3 . Квазі-частинкові зонні енергії в ільменітах CaSnO_3 та ZnSnO_3 знайдені нами вперше.

Ключові слова: Електронна структура, Функція Гріна, наближення GW, Квазічастинки.