This work presents ab initio studies of the electronic structure and optical properties of monoclinic and orthorhombic modifications of ZnSiO$_3$ and rhombohedral and tetragonal modifications of Zn$_2$SiO$_4$. All phases are wide-band-gap insulators at 0 K. The lowest part of the conduction band is more dispersive than the topmost part of the valence band. The conduction-band minimum is formed by s states and major contribution comes from the Zn-4s orbitals. From charge-density, charge-transfer, and ELF analysis it is found that the compounds are ionic. It is shown that the electron localization function is large at the interstitial sites between the O-O bond in ZnO and Zn-Zn bond in Zn$_2$SiO$_4$-t. Based on the assumption that the site preference rule of hydrogen developed in [Euro. Phys. Lett. 72(4), 569 (2005)] is valid for dielectrics, hydrogen concentration is estimated for ZnO and for Zn$_2$SiO$_4$-r. The optical properties of tetragonal phase of Zn$_2$SiO$_4$ is almost isotropic, while those of the three other phases are anisotropic. The magnitude of the absorption and reflection coefficients for all these ZnSiO$_3$ and Zn$_2$SiO$_4$ phases are so small in the energy range 0-5 eV that these materials can be regarded and classified as transparent.

Keywords: ZnSiO$_3$, Zn$_2$SiO$_4$, transparent oxides

I. INTRODUCTION

Investigation of ZnSiO$_3$ deserves attention because of their many special properties such as excellent adhesion to steel surfaces, high heat resistance, high hardness, abrasion resistance, inertness to crude and refined oils, greases, and solvents, resistance to radiation (including nuclear radiation), weather resistance etc. ZnSiO$_3$ are predominantly used for buildings, offshore constructions, and bridges. They can be used as abrasion-resistant coating with controlled electrical conductivity. The ZnSiO$_3$ are very inert and, with exception of exposure to strong acids and alkalides, do not degrade in most industrial and marine environments. It was shown in Ref. 2 that nanodispersed zinc silicates ZnSiO$_3$ co-deposited on nickel-phosphorous alloys are also corrosion resistant and high-temperature oxidation resistant. Recently, formation of a new crystalline phase of ZnSiO$_3$ is reported$^3$ upon irradiation of the nanocomposite films ZnS-SiO$_2$ with ultraviolet light. The crystalline phase is formed in the amorphous media as a result of the photoinduced reactions between ZnO and SiO$_2$.

ZnSiO$_3$ in the form of ilmenite mineral was synthesized$^{4,5}$ at 17 GPa and 1000 °C. Phase transitions of the compound at high pressures and temperatures was studied experimentally.$^4$ Cell parameters for the ilmenite phase were measured using the X-ray diffraction method under hydrostatic conditions.$^6$ The phase is not stable at atmospheric pressure and is formed as a result of transformation of clinopyroxene ZnSiO$_3$ with monoclinic structure at 10–12 GPa. The latter is formed from the reaction of willemite with quartz at about 3 GPa.$^7$

Zn$_2$SiO$_4$ is phenacite-structured also known under mineralogical name willemite. It has numerous technologically important applications such as phosphor host, crystalline phase in glass ceramics, electrical insulators, glazes, and pigments (see, e.g., Ref. 8). Because of its unique luminescent properties, wide energy band gap (5.5 eV), excellent chemical stability, Zn$_2$SiO$_4$ is one of the promising candidates for flat panel displays,$^9$–$^{14}$ X-ray or nuclear medical image receptors, X-ray to light converters coupled to optical detectors,$^{15}$ etc. Zn$_2$SiO$_4$ is formed in the heterostructure ZnO/Si because the Zn and O atoms diffuse into Si.$^{16}$–$^{18}$ ZnO deposited on silicate glass is used as a transparent conducting oxide (TCO) buffer in photovoltaic solar cells,$^{19}$ and ZnO/Si heterojunction has been investigated for monojunction solar cells.$^{20}$ By secondary ion mass spectroscopy vast interdiffusion is found between the ZnO film and the Si substrate.$^{21}$ Cathodoluminescence and glancing-angle X-ray diffraction analysis allowed to establish tetragonal modification of Zn$_2$SiO$_4$. By XRD measurements a new rhombohedral modification of Zn$_2$SiO$_4$ was found$^{22}$ at the boundary between ZnO particles and SiO$_2$ matrix. As mineral, willemite Zn$_2$SiO$_4$ belongs to a large family of naturally occurring orthosilicates.$^{23}$

The usual temperature for the formation of Zn$_2$SiO$_4$ is in the range from 700 to 1300 °C (see, e.g., Refs. 14, 21,23–26). Zn$_2$SiO$_4$ nanoparticles is prepared by solid-phase reaction methods.$^{25,26}$ However, this method does not give products with high-luminescence efficiency.$^{25}$ Alternative synthetic routes have been proposed, such as hydrothermal, polymer pyrolysis, and sol-gel methods.

The properties of coatings and mixtures of Zn$_2$SiO$_4$ powders depend on the shapes and sizes of the powder particles. So, fabrication of Zn$_2$SiO$_4$ particles with precisely-controlled morphologies is an important challenge. Ref. 27 describes synthesis of zinc-silicate-coated
microparticles with biologically controlled 3D-shapes.

Due to preference of Zn for tetrahedral rather than octahedral coordination by oxygen at low pressures, the zinc silicates crystallize into the phenacite-structure \( \text{Zn}_2\text{SiO}_4 \). At pressures above 3 GPa the mixture of \( \text{Zn}_2\text{SiO}_4 \) and \( \text{SiO}_2 \) is transformed into \( \text{ZnSiO}_3 \) with Zn atoms located in distorted octahedral coordination.\(^{4,5,28,29}\) The \( \text{ZnSiO}_3 \) clinopyroxene is found to be transformed into an ilmenite structure at 15 GPa and 1000 °C. Dependence of this reaction on temperature and pressure was studied in Refs. 28,30.

Despite the many functional useful properties of \( \text{ZnSiO}_3 \) and \( \text{Zn}_2\text{SiO}_4 \) no proper theoretical study has yet been reported. Indeed, Refs. 9 and 31 have studied \( \text{Zn}_2\text{SiO}_4 \) by the self-consistent-field multiple-scattering \( X\alpha \) cluster method. Ref. 32 has investigated fayalites \( \text{M}_2\text{SiO}_4 \) (\( \text{M} = \text{Fe} \) and \( \text{Co} \)) by GGA+\( U \) approximation, and Ref. 33 has examined the related compounds \( \text{Zn}_2\text{SnO}_4 \), \( \text{Cd}_2\text{SiO}_4 \), and \( \text{In}_2\text{CdO}_4 \) by the VASP package. However, by the \( X\alpha \) cluster method it is not possible to extract the solid-state band structure and at the time the study was carried out it was not possible to perform such calculations, because the unit cells contained too many formula units. Nowadays this problem can be solved by available \textit{ab initio} packages and modern supercomputers. The aim of the present work is to study the electronic structure and optical properties of the zinc silicates and dizinc orthosilicates. Study of the zinc silicates present much interest for semiconductor device technology, because they are formed at the interface of the \( \text{ZnO}-\text{Si} \) and \( \text{ZnO}-\text{SiO}_2 \) systems, and therefore strongly influence transport phenomena.

II. MODELS AND CALCULATIONS

A. Crystal structures

Crystal structures (Fig. 1) and lattice parameters (Table I) for orthorhombic (\( o \)), monoclinic (\( m \)) modifications of \( \text{ZnSiO}_3 \), and tetragonal and rhombohedral modifications of \( \text{Zn}_2\text{SiO}_4 \) taken from Ref. 34 are used in the present \textit{ab initio} calculations. There are two other modifications of rhombohedral \( \text{ZnSiO}_3 \) (not illustrated in Fig. 1) under the mineral name corundum \( c \) and ilmenite \( i \). Structural properties of these compounds have been analyzed more in detail in Refs. 28,29 and 30.

Two polymorphs of \( \text{ZnSiO}_3 \) have been synthesized at high pressures and temperatures (see, e.g., Ref. 35). Monoclinic \( \text{ZnSiO}_3 \) is reported to be stable above 30 kbar and 850 °C, while orthorhombic \( \text{ZnSiO}_3 \) appears to be metastable under all conditions. These characteristics are considered to be due to a peculiar behavior of Zn atoms in structures where tetrahedral coordinations predominate. In monoclinic \( \text{ZnSiO}_3 \) (Fig. 1 (b)), Zn are coordinated both octahedrally (M1) and tetrahedrally (M2).\(^{35}\) The Zn atoms at the M2 sites are not coordinated to the bridging O atoms of the \( \text{SiO}_4 \) chains.

In orthorhombic \( \text{ZnSiO}_3 \) [Fig. 1 (a)], Zn atoms at the M1 sites have irregular octahedral coordination to the O atoms. The shape of the \( \text{SiO}_4 \) chains in monoclinic and orthorhombic \( \text{ZnSiO}_3 \) is also unlike, a distinction that results the different linking of O to Zn in the two structures.

There are five pressure polymorphs of \( \text{Zn}_2\text{SiO}_4 \) designated as modifications I to V in order of increasing pressure,\(^{29}\) phase I corresponding to willemite. Phase I

---

**TABLE I: Primitive unit-cell dimensions and volumes determined experimentally\(^{34}\) and derived from the present DFT calculations by a search of the total energy minimum.**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space group</th>
<th>( a ) (( \text{Å} ))</th>
<th>( b ) (( \text{Å} ))</th>
<th>( c ) (( \text{Å} ))</th>
<th>( V_0 ) (( \text{Å}^3 ))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{ZnSiO}_3-o )</td>
<td>( \text{Pbca} )</td>
<td>18.2040</td>
<td>9.0870</td>
<td>5.2780</td>
<td>873.09</td>
<td>Expt. 35</td>
</tr>
<tr>
<td>( \text{ZnSiO}_3-m )</td>
<td>( \text{C2/c} )</td>
<td>17.0620</td>
<td>9.0205</td>
<td>5.2477</td>
<td>847.42</td>
<td>Theory</td>
</tr>
<tr>
<td>( \text{ZnSiO}_3-i )</td>
<td>( \text{R3} )</td>
<td>9.1610</td>
<td>6.7028</td>
<td>5.2960</td>
<td>221.02</td>
<td>Expt. 35</td>
</tr>
<tr>
<td>( \text{ZnSiO}_3-c )</td>
<td>( \text{R3} )</td>
<td>9.2106</td>
<td>6.6158</td>
<td>5.2528</td>
<td>214.10</td>
<td>Theory</td>
</tr>
<tr>
<td>( \text{Zn}_2\text{SiO}_4-t )</td>
<td>( \text{H2d} )</td>
<td>5.3413</td>
<td>5.3413</td>
<td>13.7536</td>
<td>268.39</td>
<td>Expt. 28</td>
</tr>
<tr>
<td>( \text{Zn}_2\text{SiO}_4-r )</td>
<td>( \text{R3} )</td>
<td>4.7469</td>
<td>4.7460</td>
<td>13.7550</td>
<td>268.30</td>
<td>Expt. 4</td>
</tr>
<tr>
<td>( \text{Zn}_2\text{SiO}_4-t )</td>
<td>( \text{R3} )</td>
<td>4.7130</td>
<td>4.7130</td>
<td>7.843</td>
<td>Theory</td>
<td></td>
</tr>
</tbody>
</table>

FIG. 1: Crystal structures of (a) orthorhombic \( \text{ZnSiO}_3-o \), (b) \( -m \), (c) corundum \( -c \), (d) ilmenite \( -i \), (e) rhombohedral \( \text{Zn}_2\text{SiO}_4-r \), and (e) \( -t \).
transforms into phase II at about 30 kbar, which is unstable above 80 kbar where it is believed to partially decompose into phase III and small amounts of ZnO. This results in somewhat non-stoichiometric composed samples and consequently phase III as well as phases IV and V are non-stoichiometric. Phase V is obtained at pressures above 130 kbar at 900 °C.

In the Zn$_2$SiO$_4$-t structure [Fig. 1 (c)] oxygen atoms join together to Si and Zn so that each oxygen of the SiO$_4$ tetrahedra is bonded to Zn atoms thus forming an integrated part of a Zn-O-Si network. The oxygen atoms are in approximately body-centered cubic arrangement in Zn$_2$SiO$_4$-t, while the Zn and Si atoms are in tetrahedral coordination to the O atoms.

In the Zn$_2$SiO$_4$-r structure [Fig. 1 (d)] the Zn and Si atoms are tetrahedrally coordinated to oxygen atoms. The Zn atoms occupy two crystallographically different sites, but the environments around these sites differ only slightly. It is assumed that Mn substitutes for Zn in Zn$_2$SiO$_4$-r.

B. Density-functional calculations

The band-structures of ZnSiO$_3$ and Zn$_2$SiO$_4$ were studied using the VASP-PAW package, which calculates the Kohn–Sham eigenvalues in the framework of the density-functional theory (DFT) within the local density approximation (LDA). The exchange and correlation energy per electron were described by the Perdew-Zunger parametrization of the quantum Monte Carlo results of Ceperley-Alder. The interaction between electrons and atomic cores was described by means of norm-conserving pseudopotentials implemented in the VASP package. The pseudopotentials are generated in accordance with the projector-augmented wave (PAW) method. The use of the PAW pseudopotentials addresses the problem of the inadequate description of the wave functions in the core region - a problem common to all pseudopotential approaches. The application of the pseudopotentials allows us to construct orthonormalized all-electron-like wave functions for the Zn-3d and -4s, Si-3s and -3p, and O-2s and -3p valence electrons. Spin-orbit coupling was not included in the present calculations.

Effective masses of conduction band (CB) electrons are calculated by:

\[
\frac{1}{m_\text{eff}(k)} = \frac{\hbar^2}{m} \frac{\partial^2 E(k)}{\partial k^2}
\]

for a direction \( k \) in the vicinity of the \( \Gamma \) point, since the CB minimum of the band dispersions of all the compounds considered were located at the \( \Gamma \) point of the Brillouin zone. The band edge energies \( E(k) \) have been extracted from DFT calculations and polynomial fitting has been performed. From the polynomial second order derivative was calculated, which was used in the effective mass calculations by Eq. 1.

C. Optical properties

The imaginary part of the dielectric function \( \epsilon_2(\omega) \) has been derived from DFT results by summing transitions from occupied to unoccupied states for energies much larger than those of the phonons:

\[
\epsilon_2^f(\omega) = \frac{V e^2}{2\pi \hbar m^2 \omega^2} \int d^3k \sum_{nn'} (\langle kn' | p_j | kn \rangle \langle kn | p_j | kn' \rangle) \times f_{kn}(1 - f_{kn'}) \delta(\epsilon_{kn'} - \epsilon_{kn} - \hbar \omega).
\]

Here \( (p_x, p_y, p_z) = p \) is the momentum operator, \( f_{kn} \) is the Fermi distribution, and \( |kn\rangle \) is the crystal wave function corresponding to the energy \( \epsilon_{kn} \) with momentum \( k \).

The real part of the dielectric function \( \epsilon_1(\omega) \) is calculated using the Kramer-Kronig transformation. The knowledge of both the real and imaginary parts of the dielectric tensor allows one to calculate other important optical spectra. In this paper we present and analyze the reflectivity \( R(\omega) \) and the absorption coefficient \( \alpha(\omega) \) calculated using the following expressions:

\[
R(\omega) = \left| \frac{\sqrt{\epsilon(\omega) - 1}}{\sqrt{\epsilon(\omega) + 1}} \right|^2,
\]

\[
\alpha(\omega) = \sqrt{2} \omega \sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega) - \epsilon_1(\omega)}.
\]

Here \( \epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \) is the complex dielectric function. The optical spectra are calculated for the energy range from 0 to 20 eV. The thus obtained optical spectra yield unbrodened functions, and consequently they exhibit more structure than the experimental constants. Lifetime broadening is simulated for Zn$_2$SiO$_4$-r. The broadening was performed by convoluting the imaginary part of the dielectric function with a Lorenzian with full width at half maximum 0.002 \( (\hbar \omega)^2 \) in eV.

III. RESULTS AND DISCUSSION

A. Ground-state properties

Figure 2 displays the total energy \( (E_{\text{tot}}) \) calculated within LDA as a function of the unit cell volume \( (V/V_0) \). The symmetries of all phases considered remain the same for both relaxed and unrelaxed lattices. The minima \( E_{\text{tot}}^{\text{min}} \) in \( E_{\text{tot}}(V/V_0) \) are taken as the equilibrium volume. Lattice parameters derived from the DFT calculations are shown in Table I together with experimentally determined ones. Analysis of the Table I shows that accuracy of the calculated lattice parameters is \( < 3.2 \% \) for ZnSiO$_3$-o and -m. For ZnSiO$_3$-i, Zn$_2$SiO$_4$-r and Zn$_2$SiO$_4$-t the calculated and experimentally determined lattice parameters almost coincide.

\( E_{\text{tot}}^{\text{min}} \) for ZnSiO$_3$-i is found to be considerably larger compared to that of the other ZnSiO$_3$ phases, so it was
Experimental findings of Ref. 35, which stated that ZnSiO
not included into Fig. 2. However, total energy minimum of ZnSiO$_3$-c, -m, and -o are close to each other. Among them ZnSiO$_3$-c and -o are less stable than ZnSiO$_3$-m. The dependence $E_{\text{tot}}(V/V_0)$ for ZnSiO$_3$-m crosses minimum of that for ZnSiO$_3$-o. Consequently, once the phase ZnSiO$_3$-o is obtained, it can automatically be transformed into ZnSiO$_3$-m. This result is consistent with experimental findings of Ref. 35, which stated that ZnSiO$_3$-o is metastable under all conditions.

Analysis of Fig. 2(b) shows that among the Zn$_2$SiO$_4$ compounds considered Zn$_2$SiO$_4$-r is more stable than ideal and defective Zn$_2$SiO$_4$-t. A defective Zn$_2$SiO$_4$-t lattice was created by shifting one of the Zn atoms into an interstitial position. Then the lattice was relaxed. It follows from Fig. 2(b) that such a defective lattice is not stable. Comparing Fig. 2(a) with Fig. 2(b) one can see that ZnSiO$_3$ phases considered are more stable than the Zn$_2$SiO$_4$ ones. From the studies of the ground-state properties it is concluded that upon analysis of the electronic structure and optical spectra major attention should be focused into the following phases ZnSiO$_3$-o, ZnSiO$_3$-m, Zn$_2$SiO$_4$-r, and Zn$_2$SiO$_4$-t, which are more stable than the others.

**B. Band structure according to density-functional calculations**

For studies of the optical properties knowledge of the interband transitions is needed. From this point of view analysis of the electronic structure is an important problem. Band structures along the high-symmetry directions in the Brillouin zone are presented in Fig. 3. Analysis of the Fig. 3 shows that the interesting feature in properties of the VB of ZnSiO$_3$-o, ZnSiO$_3$-m, ZnSiO$_3$-c, and Zn$_2$SiO$_4$-r is the presence of a flat band in the topmost VB, whereas the bottommost CB separated from the VB by a wide gap is more dispersive. This feature is typical for TCO of n-type conductivity (see, e.g., Refs. 9,31–33,46–48). It shows to predominant ionic type of the chemical bonding of the compounds and the valence electrons located at the topmost VB are tightly bounded to the O atoms. It follows from analysis of partial density of states (DOS) in the following Subsection III C, that the topmost VB states consist of mainly the O-2p orbitals. Consequently, holes are almost immobile and their contribution to current transport is expected to be considerably smaller than that of CB electrons. However, the states at the CB minimum are much more dispersive than the topmost VB states. Consequently, small carrier effective masses, high electron mobility and, respectively, high n-type conductivity, and the Burstein-Moss shift or shift of the optical absorption edge with doping are expected. The high dispersion comes out from a strong hopping between neighboring Zn sites. This statement shall be justified in Subsection III C by analysis of the partial DOS for the very bottom CB. These are one of the most important electronic band structure features of a host TCO material. Hence these materials can be regarded as very promising candidates for TCO.

As seen from Fig. 3 the valence band (VB) states of ZnSiO$_3$-i and Zn$_2$SiO$_4$-t are more dispersive compared to other compounds considered. It indicates that covalency plays an important role in chemical bonding of ZnSiO$_3$-i and Zn$_2$SiO$_4$-t. Furthermore, contribution of holes to current transport can be significant. However, as discussed upon studies of the ground-state properties, ZnSiO$_3$-i is less stable compared to the other ZnSiO$_3$ phases.
It should be noted that the bands at the topmost VB of ZnSiO$_3$-$\alpha$, ZnSiO$_3$-$m$, Zn$_2$SiO$_4$-$r$, and Zn$_2$SiO$_4$-$t$ are very close to each other and are very flat [Fig. 3]. Consequently, it is hard for the eye to identify the maximum in the VB. Therefore, for more detailed information about the states at the VB maximum fine structure is plotted in Fig. 4. It presents the band dispersion in Fig. 3 expanded in an energy scale around the band gap. From this figure it is clear that for all phases of the zinc silicates considered the CB minimum is located at the $\Gamma$ point. However, the VB maximum is located at different $k$ points. The band dispersion of ZnSiO$_3$-$\alpha$ is complicated. The VB maximum is located in the range from $\Gamma$ point to a location between the $X$ and $S$ points. ZnSiO$_3$-$m$, ZnSiO$_3$-$i$, ZnSiO$_3$-$c$ and Zn$_2$SiO$_4$-$r$ are found to be indirect band gap compounds with the VB maximum located around $Z$ point (ZnSiO$_3$-$m$), $X$, $P$ and $N$ point (ZnSiO$_3$-$i$ and ZnSiO$_3$-$c$). The Zn$_2$SiO$_4$-$r$ has a direct band gap with CB minimum and VB maximum located around the $\Gamma$ point. Topmost VB of Zn$_2$SiO$_4$-$t$ is almost dispersionless within whole Brillouin zone. The large indirect band gap for ZnSiO$_3$-$m$, ZnSiO$_3$-$i$, and ZnSiO$_3$-$c$ indicates that small absorption is to be expected. This result has been confirmed by studies of optical spectra for these compounds.

Band gap values ($E_g$) for all the compounds studied are listed in the Table II. An experimental $E_g$ is widely available only for rhombohedral Zn$_2$SiO$_4$-$r$. It is in the range from 5.5 to 6.262 eV. The band gap 4.36 eV estimated from the band diagram for Si-ZnO heterojunction derived from the XPS studies is probably, of Zn$_2$SiO$_4$-$t$. Experimentally measured band gap for the other ZnSiO$_3$ and Zn$_2$SiO$_4$ phases are not yet available.

The value of $E_g$ calculated in the present DFT studies for ZnSiO$_3$-$\alpha$ and -$m$ phases exceeds 3.5 eV, while that for Zn$_2$SiO$_4$-$r$ is only 2.83 eV. Since the band gaps calculated by DFT within LDA are likely to be about 50% smaller than actual experimental values, the real band gaps for these zinc silicates may be around 5.0 eV, which in turn would imply that the materials are transparent across the entire visible spectrum. Hence, these materials carry one of the most desirable properties for the TCO’s. Although the calculated direct band gap of ZnSiO$_3$-$i$ is small (2.2166 eV), it can surely be increased upon doping (Burstein-Moss shift) or by structural defects as it shall be demonstrated in Subsection III.G.

C. Density of states

To explore the origin of the states in the band structure of zinc silicates the density of states (DOS) has been analyzed. Figure 5 presents total DOS for ZnSiO$_3$-$\alpha$, ZnSiO$_3$-$m$, ZnSiO$_3$-$i$, ZnSiO$_3$-$c$, Zn$_2$SiO$_4$-$r$ and Zn$_2$SiO$_4$-$t$ phases. The DOS exhibit sharp peaks, since we have not include the lifetime broadening. It is seen that the VB consists of two major bands. Upper one is very broad. It is located in the energy range around -9.5 to 0.0 eV. The lower band is located in the energy range from -20 to -17 eV. It is narrow and is split into two sharp subbands.

To get more insight into the VB spectra, angular momentum and site decomposed DOS has been plotted in Fig. 6. It is seen that the lowest $s$ band is contributed mainly from the O-$2s$. Smaller contribution comes from hybridized Si-3s and -3p orbitals. Analysis of the partial DOS shows that the topmost VB can be divided into the parts: The lowest part is basically contributed from the Si-3s-orbitals. This result shows strong hybridization of the Si-3s and 3p orbitals. This feature is the property of the Si atoms only. The sharp and high-intensity band located at higher energy is seen to originate from the Zn-3d electrons. The third, topmost part of the VB is the hybrid of the Zn-3d and the O-2p states, while contribution of the Si 3p states is negligible. This result indicates that the Si-O bond is more or less pure ionic. However, it is interesting to note, that the Zn-O bond is covalent. Consequently, deviation of Zn and/or O atoms from stoichiometry is expected to change the

<table>
<thead>
<tr>
<th>Phase</th>
<th>$E_g$ (eV)</th>
<th>$E_g^{Exp}$ (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSiO$_3$-$\alpha$</td>
<td>3.5006</td>
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</tr>
<tr>
<td>ZnSiO$_3$-$m$</td>
<td>3.6762</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnSiO$_3$-$c$</td>
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<td></td>
</tr>
<tr>
<td>ZnSiO$_3$-$i$</td>
<td>2.2166</td>
<td>5.5</td>
<td>Ref. 11</td>
</tr>
<tr>
<td>Zn$_2$SiO$_4$-$r$</td>
<td>2.8299</td>
<td>5.3</td>
<td>Ref. 49</td>
</tr>
<tr>
<td>Zn$_2$SiO$_4$-$t$</td>
<td>2.7950</td>
<td>6.15</td>
<td>Ref. 21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.262</td>
<td>Ref. 21</td>
</tr>
</tbody>
</table>

TABLE II: Band gaps of the zinc silicates ZnSiO$_3$ and Zn$_2$SiO$_4$ calculated by DFT within the LDA and measured experimentally.
The Fermi level is set at zero of energy. This result is obtained for all the compounds considered. The edge of CB is formed by the $s$ states. As is well known, the $s$-type character of the CB edge is one of the most important features of the TCO materials in order to give the electrons high mobility and conductivity. Major contribution to the CB edge comes from the Zn-$4s$ orbitals. It shows strong hopping between two neighboring Zn sites. Contribution of the O-$2s$ orbitals to the DOS is smaller than those of the Zn-$4s$. The smallest contribution comes from the Si-$3s$ orbitals. These analysis shows that all these elements can provide a path for electrical conductivity in the crystal. Among them, the Zn-$4s$ orbitals play an important role in the electrical conductivity of all the zinc silicates considered. Based on smaller contribution of the Si-$3s$ and O-$2s$ orbitals to the CB edge than the Zn-$4s$ orbitals it is thought that the SiO$_2$ layers may play little role in scattering electrons that move within the ZnO layer. So, in the zinc silicates heavily doped by ions substituting one of the elements of the SiO$_2$ layer, the reduction in mobility can be restrained. Experimental research is required to verify this suggestion by establishing the relationship between the electrical properties and concentration of dopant ions.

**D. Conduction band effective masses**

As noted in the analysis of the band dispersions [Fig. 3] the lowest CB states are much more dispersive than the topmost VB states. Consequently, CB electrons are lighter than holes and he latter can be ruled out from conductivity. The reason is that the valence electrons are tightly bound into O atoms resulting in almost flat
VB states. So, hole effective masses were not calculated.

The calculated CB electron effective masses are presented in Table III. Analysis shows that the masses for ZnSiO$_3$-o and Zn$_2$SiO$_4$-r are almost isotropic, while those for the other zinc silicates considered are anisotropic. Hence, electron mobility and conductivity of ZnSiO$_3$-o and Zn$_2$SiO$_4$-r are expected to be isotropic, while those for ZnSiO$_3$-m and Zn$_2$SiO$_4$-t are anisotropic. At present there are no experimental data to compare the theoretical results.

Analysis of the magnitudes of the CB electron masses shows that the masses of ZnSiO$_3$-o, ZnSiO$_3$-m and Zn$_2$SiO$_4$-t are of the same magnitude, whereas those of Zn$_2$SiO$_4$-r are considerably larger, which indicates that the latter compound is not suitable for TCO. The CB electron masses computed in the present work are almost two times larger than those of Zn$_2$SnO$_4$, Cd$_2$SnO$_4$, and CdIn$_2$O$_4$ (Ref. 33).

### Table III: Effective masses of CB electrons (in units of the free-electron mass $m_0$) for ZnSiO$_3$-o, ZnSiO$_3$-m, Zn$_2$SiO$_4$-r and Zn$_2$SiO$_4$-t.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mass (Γ−X)</th>
<th>Mass (Γ−A)</th>
<th>Mass (Γ−F)</th>
<th>Mass (Γ−N)</th>
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</thead>
<tbody>
<tr>
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<td>0.3351</td>
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<td>Zn$_2$SiO$_4$-r</td>
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<td>0.4695</td>
<td>1.2400</td>
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</table>

#### E. Charge-density, charge-transfer, and electron localization function analysis

For more detailed understanding of the bonding nature, charge-density, charge-transfer, and electron localization function (ELF) analysis have been performed. Figures 8 (a)–(c) present such analysis for Zn–O and Si–O bonds of Zn$_2$SiO$_4$-r. For comparison Zn–O bonding is analyzed in Figures 8 (d)–(f) for ZnO of wurtzite structure to see how inclusion of Si into the ZnO matrix changes the charge distribution, charge transfer and ELF. The other compounds Zn$_2$SiO$_4$-t, ZnSiO$_3$-o, ZnSiO$_3$-m, ZnSiO$_3$-l, and ZnSiO$_3$-c exhibit the features similar to Zn$_2$SiO$_4$-r. It follows from the charge-distribution analysis that the highest charge density is resided in the immediate vicinity of the nuclei and that the compounds are more ionic. The charge around Zn atoms is larger than that around Si. It indicates to more ionic nature of the Si–O bonds compared to those of the Zn–O. Some covalency is present in the latter. This result is consistent with analysis of the angular momentum and site-projected DOS in Subsection III C. The charge around O and Si atoms is not spherical, which indicates that there are different types of ions. Inspection of charge density for ZnO shows that there is some charge in between the two nearest O atoms.

Figures 8 (b) and (e) display the charge transfer, which is substraction of the electron distribution of free atoms from that of the compound. This illustration shows that the charge has been transferred from the Zn and Si to the O atoms further confirming the above conclusion regarding ionic nature of the zinc silicates understudied. Compared to Si sites, Zn sites contain more charge, which is consistent with the charge density and DOS analysis. However, near the Zn, Si and O sites, magnitude of the transferred charge is varied in different directions of the crystal. It shows that there is small amount of covalency. There is some amount of charge located in between the two nearest O atoms of ZnO [Fig. 8 (e)]. This feature is the property of ZnO only and non of the zinc silicates considered posses it.

The ELF is one of the useful tools to characterize chemical bonding in solids. It is a measure for the probability distribution of paired electrons. Compared to charge distribution, it is able to better distinguish different bonding situations for electrons. For more information about capabilities of this tool see, e.g. Refs. 50–52 and Refs therein. Figures 8 (c) and (f) presents the calculated ELF plot. Analysis shows that the ELF value is very low at the Si. Higher value of ELF is available around Zn atoms and the very high ELF is at O atoms.

In ZnO there is a spot located in between two O atoms where ELF indicates a maximum value around 0.52 (Fig. 8 (c)). Consequently, the electrons in this spot are well paired in nature. Extrapolating the site preference rule of hydrogen in metal, alloy, and intermetallic frameworks to dielectrics these sites are suggested to be the candidates for locating a H, Li, Cu, or Na atom, because the preferable site for the latter in a lattice is the one where there is no atom, but there is some amount of charge. The charge would participate in forming the stable Is$^2$ paired electron, thus completing the valence shell of H atom. The high ELF value in the interstitial region exceeding 0.5 can be the indicator that the site has enough potential to complete the valence shell of the incorporated H atom. Knowing the unit cell volume for and ZnO ($V_0 = 47.62$ Å$^3$, Ref. 34), and assuming that one hydrogen atom occupies the site with high ELF value one can estimate the maximal value of the hydrogen concentration ($N_H$), which can be in-
Optical spectra of (a) ZnSiO$_3$-$o$ and (b) ZnSiO$_3$-$m$, and of (c) Zn$_2$SiO$_4$-$t$ and (d) Zn$_2$SiO$_4$-$t$. For the latter the directions corresponding to the electric field parallel $E$||c (dotted lines) and perpendicular $E$⊥c (solid lines) to the crystallographic c axes are considered. For the other compounds considered the directions along $E$⊥a (solid lines), $E$⊥b (dotted lines), and $E$⊥c (dashed lines) are considered.

corporated into the matrix. Such an estimation shows that $N_H = 2.1 \times 10^{22}$ cm$^{-3}$ for ZnO. No interstitial site with high ELF value was found between the Si–O bonding. Furthermore, this feature is not found in zinc silicates. The charge-density, charge-transfer and ELF analysis show that except Zn–O and Si–O, there is also O–O.

**F. Optical properties**

There are no published data on the optical spectra of the zinc silicates. The problem is studied in this work. We hope that our calculated optical spectra will motivate experimental studies. Figure 9 displays the real ($\varepsilon_1(\omega)$) and imaginary ($\varepsilon_2(\omega)$) part of the dielectric function, absorption ($\alpha(\omega)$) and reflectivity ($R(\omega)$) coefficients. In order to understand the optical anisotropy of the zinc silicates, three components of the dielectric function are calculated for ZnSiO$_3$-$o$, six components for ZnSiO$_3$-$m$, two components for Zn$_2$SiO$_4$-$t$, and six components for Zn$_2$SiO$_4$-$t$. For simplicity of analysis, only three diagonal components of the dielectric function are considered for ZnSiO$_3$-$m$ and Zn$_2$SiO$_4$-$t$. These three components are directed along the crystallographic a, b and c axes. The two components for Zn$_2$SiO$_4$-$t$ correspond to the electric field parallel $E$||c and perpendicular $E$⊥c to the crystallographic c axes.

Optical spectra are found to be anisotropic for all the compounds considered except Zn$_2$SiO$_4$-$t$, for which all the optical spectra are found to be more or less isotropic.

The anisotropy is well pronounced in ZnSiO$_3$-$m$ and Zn$_2$SiO$_4$-$t$ for which all the optical spectra along the direction $E$||c are much smaller than the other directions. Furthermore, a similarity is evident in the absorption and reflectivity spectra between these two compounds (Fig. 9). That is the reflectivity coefficient changes non-monotonically with increasing the energy. It has a maximum at $E \approx 10$ eV. For $E > 10$ eV, $R(\omega)$ decreases with increasing the energy. As discussed above, the optical spectra for $E$||c is much smaller than those for $E$||a and $E$||b. Also, along the directions $E$||a and $E$||b all the optical spectra are more or less isotropic. For the ZnSiO$_3$-$o$ the optical spectra except reflectivity, are also isotropic. The reflectivity spectra shows anisotropy at high energies $E \leq 13$ eV.

For $E \geq 7.5$ eV the absorption coefficient $\alpha(\omega)$ increases with increasing the energy for all the compounds considered. For ZnSiO$_3$-$o$, $\alpha(\omega)$ has a maximum at $E \approx 12.5$ eV and it decreases with increasing the energy at $E < 12.5$ eV. For the other zinc silicates $\alpha(\omega)$ stays to be almost the same for $E \geq 10.0$ eV.

Analysis of the optical spectra shows that the values of the real part of the dielectric function $\varepsilon_2(\omega)$, absorption $\alpha(\omega)$, and reflectivity $R(\omega)$ are two small in the energy range 0–5 eV. It indicates that the compounds considered present interest as TCO.

**G. Electronic structure of Zn interstitials in Zn$_2$SiO$_4$-$t$**

As demonstrated in Subsection III C major contribution to the lowest CB of the zinc silicates comes from the Zn-4s states. Furthermore, Zn-4d states contributes significantly to the topmost VB. Consequently, VB maximum and CB minimum should change drastically on the Zn-related structural point defects. Although in the Subsection III A it was shown that the defective structure is less stable compared to the ideal one [Fig. 2], in this subsection we shall discuss electronic structure, charge density, charge transfer and ELF analysis, as well as optical spectra of the defective Zn$_2$SiO$_4$-$t$ structure to demonstrate some interesting features coming out from structural point defects. One Zn interstitial in a unit cell of Zn$_2$SiO$_4$-$t$ shall be considered.

Figure 10 displays band dispersion for the defective Zn$_2$SiO$_4$-$t$ with the Zn interstitial. It is seen that the lowest free-electron-like CB state has been split from the CB to 0.60 eV and from VB to 1.31 eV. As it was shown in Sec. III C upon discussion of the partial DOS, this feature is related to origin of the lowest CB states originating mainly from the strongly hybridized Zn-4s, Si-3s, and O-2s states. Hence, the structural point defects can form an intermediate band. Width of the band is 2.17 eV and it is dispersive. Furthermore, effective mass of electrons is around 0.46$m_0$. These features indicate that electrons of this band can significantly contribute to conductivity. If by doping the intermediate band shall partially be filled.
with electrons, then it can be regarded as metallic band. So, the intermediate bands can be formed not only by impurities, but also by structural point defects.

As noted in Ref. 46 separation of the lowest highly dispersive CB minimum state is preferable to satisfy one of the important features of the band structure such that the plasma frequency should be below the visible range. From this point of view separation of the CB minimum and formation of the intermediate band can lead to lowering the plasma frequency, since it is proportional to the largest energy of the intraband transition.

The Zn interstitial has increased width of the topmost VB from 7.5 corresponding to ideal lattice to 10.0 eV and split two localized bands of the ideal cell in the lowest VB into three localized bands. For detailed knowledge of the defect-induced changes of the band structure comparative analysis of the total DOS and angular momentum and site projected DOS shall be performed for ideal and defective Zn$_2$SiO$_4$-t [Fig. 11 (a) and (b)].

It is seen that Si-$3s$ and -$3p$ states still contribute significantly to the lowest VB. However, compared to the ideal lattice the bands have been split and they have been converted from two narrow high-intensity localized bands into three low-intensity localized bands. At the topmost VB the Si-$3s$ and -$3p$ bands are considerably hybridized. Furthermore, distinct from the ideal lattice, which at the topmost VB had some contribution from Zn and no contribution from Si, the defective lattice has contribution from Si-$3p$ and no contribution from Zn atoms. It means that the nature of the Si–O and Zn–O bonds have been changed. The Si–O bonds, which in ideal lattice was almost pure ionic, possessed some covalency, whereas the Zn–O bonds, which in ideal lattice had some covalency become almost pure ionic.

Figure 12 shows the dielectric response functions $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$, absorption coefficient $\alpha(\omega)$ and reflectivity $R(\omega)$ for the defective Zn$_2$SiO$_4$-t. Two peaks at 1.65 and 2.47 eV are well defined in the spectral distribution of the dielectric response. These peaks can be ascribed to the optical transition from the VB to the intermediate band. The next The peak at around 3.98 eV corresponds to the VB to CB transition. In the absorption spectra the former two peaks are smaller than latter. It shows that the optical transition from VB to CB is stronger. In the reflectivity spectra magnitude of these peaks are comparable. Since Zn$_2$SiO$_4$-t is undoped, there are no electrons in the intermediate band. Furthermore, illumination intensity considered in the present calculations corresponds to one sun. Consequently, the transition from the intermediate band to CB is negligible.

Once Zn interstitials have changed the band structure and optical properties, they are expected to influence the chemical bonding also. Below charge-density, charge-transfer, and ELF analysis have been performed for the defective for Zn$_2$SiO$_4$-t Compared to ideal lattice,
the bonding Zn-O have been modified significantly. Figure 13 demonstrates these features. Charge-distribution [Fig. 13(a)] and charge transfer [Fig. 13(b)] analysis show that the highest charge density is resided in the vicinity of the nuclei. However, distinct from the ideal lattices, some amount of charge is located in between the two nearest Zn atoms. One of the Zn atoms is the Zn interstitial. Analysis of ELF shows that in between the two Zn atoms there is a spot where ELF indicates a maximum value around 0.52. So, one can conclude that the electrons in this spot is paired well enough. According to the site preference rule this site can be the candidates for locating a H or other impurity atom with unpaired electron, which participates in forming the stable $1s^2$ pair electron and completes the valence shell of the H atom. Knowing the unit cell volume for $\text{Zn}_2\text{SiO}_4$ [Table I] maximal value of the hydrogen concentration ($N_H$) is estimated to be equal to $N_H = 3.2 \times 10^{21}$ cm$^{-3}$. No interstitial site with high ELF value was found between the Si-O bonding. Furthermore, this feature is not found in ideal lattices of the compounds considered in this paper.

IV. CONCLUSION

This work presents ab initio studies of electronic structure and optical properties of ZnSiO$_3$-o and -m, and Zn$_2$SiO$_4$-t and -t. By a search of the total energy minimum the equilibrium volume is found, which is in good agreement with experimentally determined one. The DFT calculations of the electronic structure and optical properties of the zinc silicates have been performed using the experimentally determined lattice parameters. It is shown that all the compounds considered are wide band gap, lowest CB is dispersive, while the topmost VB is dispersionless. Furthermore, the lowest CB is formed of the valence s orbitals of the Zn, Si, and O atoms and major contribution comes from the Zn-4s orbitals. The lowest one among the peaks in the dependence of the partial DOS of the Zn-4s, Si-3s, and O-2s orbitals on energy is located at the same energy. This result is valid for all the zinc silicates studied. It is found that the Si-3p orbitals contribute to the lowest valence band, while the Si 3s-like orbitals contribute to the topmost valence band of the compounds. Analysis of the density of states, charge-density, charge-transfer, and ELF shows that the compounds understudied are ionic. It is found that ELF value is high in the interstitial sites between the O-O bond in ZnO and Zn-Zn bond in the defective Zn$_2$SiO$_4$-t. Suggesting that the site preference rule of hydrogen in metal, alloy, and intermetallic frameworks of Ref. 50 is also valid for dielectrics, the interstitial sites with large ELF value are concluded to be the candidates for locating a H atom. Charge of the interstitial sites would participate in forming the stable $1s^2$ paired electron and complete the valence shell of H atom. Assuming that one hydrogen atom occupies the interstitial site, hydrogen concentration is found $N_H = 2.1 \times 10^{22}$ cm$^{-3}$ for ZnO and $N_H = 3.2 \times 10^{21}$ cm$^{-3}$ for Zn$_2$SiO$_4$-t. Optical properties are found to be almost isotropic for Zn$_2$SiO$_4$ in bodycentered tetragonal phase, while they are anisotropic for the other compounds considered. In the energy range from 0.0 to 5.0 eV, absorption and reflectivity coefficients are found to be very small. Based on the above analysis it is concluded that the zinc silicates can be regarded as potential candidates for TCO. From DFT calculations of electronic structure of the Zn interstitials in Zn$_2$SiO$_4$-t it is concluded that point structural defects can modulate the band structure, chemical bonding, and optical properties and form an intermediate band. Electronic transitions from the VB to the intermediate band was found in the optical spectra.

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1. J. M. Keijman, in PCE ’99 Conference (Brighton, United Kingdom, 1999).