Materials Research Express

PAPER

DFT-investigation on anisotropy degree of electronic, optical, and mechanical properties of olivine ZnRE$_2$S$_4$ (RE = Er, Tm) compounds

M Batouche$^1$, T Seddik$^{1,4}$, S Üğur$^1$, G Üğur$^1$, S Messekine$^3$, Tuan V Vu$^{1,4}$ and O Y Khyzhun$^3$

$^1$ Laboratoire de Physique Quantique et de Modélisation Mathématique, Université de Mascara, Mascara-29000, Algeria
$^2$ Department of Physics, Faculty of Science, Gazi University, Ankara 06500, Turkey
$^3$ Division of Computational Physics, Institute for Computational Science, Ton Duc Thang University, Ho Chi Minh City, Viet Nam
$^4$ Faculty of Electrical & Electronics Engineering, Ton Duc Thang University, Ho Chi Minh City, Viet Nam
$^5$ Frants eych Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, 3 Krzyzhansky Street, UA-03142 Kyiv, Ukraine

E-mail: batouchemohammed@yahoo.fr, tahl.seddik@univ-mascara.dz, seddik.t@yahoo.fr, vuvantuan@tdtu.edu.vn and khyzhun@ipms.kiev.ua

Keywords: ab-initio calculations, electronic properties, optical properties, elastic properties, anisotropy, optical materials

Abstract

Using PP-APW method the electronic, optical and mechanical anisotropy of ZnRE$_2$S$_4$ (RE = Er, Tm) olivine compounds was investigated. The calculated unit cell parameters are in good agreement compared to the experimental ones. In addition, the study of electronic properties reveals that ZnEr$_2$S$_4$ and ZnTm$_2$S$_4$ are semiconductors with a direct bandgap of about 2.37 eV and 2.35 eV, respectively. The optical constants such as refractive index, reflectivity, and absorption coefficient have been calculated and analyzed. These constants show a clear anisotropy in the UV region for both compounds caused by the different electron polarizability in $x$-, $y$- and $z$-direction. Moreover, the elastic constants are estimated for the first time for ZnEr$_2$S$_4$ and ZnTm$_2$S$_4$ indicating that the compounds are mechanically stable and reveal ductility behavior. The direct bandgap, optical absorption, and mechanical stability make ZnEr$_2$S$_4$ and ZnTm$_2$S$_4$ promising candidates for optoelectronic application.

1. Introduction

Ternary lanthanide chalcogenides MRE$_2$Ch$_4$ (M: transition metal) have been a subject of intense interest not only owing to their complex structures, but also due to diversity of their physical properties revealing semiconducting nature [1, 2], optical properties [3–5], good thermal resistance [6], thermoelectricity [7–9], magnetic properties [10–17], mechanical durability and high corrosion resistance [18]. Such properties make them suitable candidates for diverse applications such as photocatalysis, photoelectrochemical solar cells, infrared windows and photoconductors [19–21].

In addition, the MRE$_2$Ch$_4$ compounds adopt several different structure types [1, 2] which contain a combination of $d$- and $f$-elements. Among them, ternary ZnRE$_2$S$_4$ (RE = Er, Tm) sulfides are known to exist that were synthesized for the first time by Yim et al [1] and latter by Vollebregt and Ijdo [22]. In accordance to data of Refs. [1, 22], ZnRE$_2$S$_4$ (RE = Er, Tm) sulfides crystallize in the olivine structure. Moreover, Lau et al [15] investigated the magnetic properties of the olivine ZnRE$_2$S$_4$ (RE = Er, Tm) compounds indicating that neither ZnEr$_2$S$_4$ nor ZnTm$_2$S$_4$ possesses a magnetic long-range order beyond $T = 1.8K$. This behavior is possibly due to their low-dimensional structure or the frustrating effect of the triangular geometry in these materials [15]. However, in spite of the fact that these two compounds belong to the fascinating chalcogenide MRE$_2$Ch$_4$ family, until now there exist a restricted number of works on the physical properties of these compounds. Therefore, it is very interesting to study the physical properties of the olivine ZnRE$_2$S$_4$ (RE = Er, Tm) materials to retrieve more information on their electronic, optical and elastic properties.
On the other hand, owing to the low-dimensional olivine ZnRE$_2$S$_4$ (RE = Er, Tm) structure and combined existence of $d$- and $f$-elements, anisotropic behavior of the physical properties is often expected to exist in these compounds. Hence it is very important to investigate the anisotropic effect on electronic, optical and elastic properties of ZnRE$_2$S$_4$ (RE = Er, Tm) compounds. For this reason, we present in this work a detailed study giving better understanding the electronic, optical and elastic properties of ZnRE$_2$S$_4$ (RE = Er, Tm) olivine, using pseudo-potentials projected augmented wave (PP-PAW) method based on density functional theory (DFT).

2. Computational method

The present calculations were performed via the PP-PAW method [23, 24] based on the DFT approach as implemented in the MedeA software environment [25, 26]. The exchange-correlation potential was treated through the generalized gradient approximation (GGA-PBE) parameterized by Perdew et al [27]. The convergence is accomplished using 6 × 4 × 4 $k$-points mesh in the Brillouin zone by means of Monkhorst–Pack method [28] and a kinetic energy cut-off of about 520eV with total energy convergence threshold of $10^{-5}$ eV. Moreover, the elastic constants and related mechanical properties were estimated utilizing the MT module of MedeA [29] based on the stress-strain approach.

3. Results and discussion

3.1. Structural properties

The ZnRE$_2$S$_4$ (RE = Er, Tm) olivine sulfides crystallize in orthorhombic structure with space group $Pnma$ (No = 62) [30] that is presented in figure 1. This structure is based on a hexagonal close packing of S atoms with three Wyckoff positions S1 at ($u$, 1/4, $w$), S2 at ($u$, 1/4, $w$) and S3 at ($u$, $v$, $w$), whereas the Er/Tm atoms are located in octahedral interstices with two different positions: RE1 at (0, 0, 0) and RE2 at ($u$, 1/4, $w$). The Zn atoms are positioned in tetrahedral interstices ($u$, 1/4, $w$) in such a way that each S atom has one Zn and three Er/Tm neighbors [31]. The calculated equilibrium unit-cell parameters $a$, $b$ and $c$ for ZnEr$_2$S$_4$ and ZnTm$_2$S$_4$ are listed in Table 1 together with the available experimental data [1, 22]. From data of Table 1, it is clear that the obtained lattice parameters for both materials are in reasonable agreement compared to the experimental results. The difference between the estimated unit-cell values and the experimental values is less than 1%. Furthermore, the obtained atomic coordinates (Table 2) show reasonable agreement compared to the measured ones [22].
3.2. Electronic properties

Figure 2 presents the calculated band structure of ZnRE$_2$S$_4$ (RE = Er, Tm) compounds along with special symmetry directions in the Brillouin Zone, using GGA-PBE approximation. From figure 2, one can see that the valance band maximum (VBM$_a$) and the conduction band minimum (CBM$_i$) are positioned at $\Gamma$ (0, 0, 0) point, with energy bandgap between them of about 2.37 eV and 2.35 eV for ZnEr$_2$S$_4$ and ZnTm$_2$S$_4$, respectively. Consequently, both materials are direct bandgap semiconductors. The estimated band gap value of ZnTm$_2$S$_4$ is

Table 1. The calculated unit cell parameters $a$, $b$ and $c$ (in Å) and the $(c/a, b/a)$ ratios of ZnRE$_2$S$_4$ (RE = Er, Tm) in comparison with the measured ones.

|        | $a$    | $b$    | $c$    | $c/a$  | $b/a$  |
|--------|--------|--------|--------|--------|--------|
| ZnEr$_2$S$_4$ | 13.450 | 7.824  | 6.304  | 0.468  | 0.581  |
| Expt.  | 13.344$^{ab}$ | 7.766$^{ab}$ | 6.299$^{ab}$ |        |        |
| ZnTm$_2$S$_4$ | 13.393 | 7.790  | 6.293  | 0.469  | 0.581  |
| Expt.  | 13.227$^{a}$, 13.301$^{b}$ | 7.734$^{a}$, 7.747$^{b}$ | 6.263$^{a}$, 6.281$^{b}$ |        |        |

Notes.

$^a$ [1].
$^b$ [22].

Table 2. Atomic coordinates of ZnRE$_2$S$_4$ (RE = Er, Tm) crystals.

|        | ZnEr$_2$S$_4$ | ZnTm$_2$S$_4$ |
|--------|---------------|---------------|
|        | $x$           | $y$           | $z$           | $x$           | $y$           | $z$           |
| Zn     | 0.4086        | 0.25          | 0.07234       | 0.4085        | 0.25          | 0.0885        |
|        | 0.406$^a$     | 0.00$^a$      | 0.0736$^a$    | 0.4074$^a$    | 0.00$^a$      | 0.0859$^a$    |
| RE1    | 0.2349        | 0.25          | 0.5022        | 0.2349        | 0.25          | 0.5027        |
|        | 0.2227$^a$    | 0.5085$^a$    | 0.23351$^a$   | 0.23351$^a$   | 0.5056$^a$    | 0.23351$^a$   |
| S1     | 0.4095        | 0.25          | 0.7234        | 0.4097        | 0.25          | 0.7228        |
|        | 0.4084$^a$    | 0.7234$^a$    | 0.41$^a$      | 0.41$^a$      | 0.721$^a$     | 0.721$^a$     |
| S2     | 0.0705        | 0.25          | 0.2558        | 0.0710        | 0.25          | 0.2548        |
|        | 0.0531$^a$    | 0.2789$^a$    | 0.0721$^a$    | 0.0721$^a$    | 0.23$^a$      | 0.23$^a$      |
| S3     | 0.3320        | 0.0124        | 0.2562        | 0.3317        | 0.0116        | 0.2372        |
|        | 0.3373$^a$    | 0.0332$^a$    | 0.2222$^a$    | 0.3318$^a$    | 0.0129$^a$    | 0.2379$^a$    |

Notes.

$^a$ [22].

3.2. Electronic properties

Figure 2 presents the calculated band structure of ZnRE$_2$S$_4$ (RE = Er, Tm) compounds along with special symmetry directions in the Brillouin Zone, using GGA-PBE approximation. From figure 2, one can see that the valence band maximum (VBM$_a$) and the conduction band minimum (CBM$_i$) are positioned at $\Gamma$ (0, 0, 0) point, with energy bandgap between them of about 2.37 eV and 2.35 eV for ZnEr$_2$S$_4$ and ZnTm$_2$S$_4$, respectively. Consequently, both materials are direct bandgap semiconductors. The estimated band gap value of ZnTm$_2$S$_4$ is
underestimated somewhat compared to the optical gap of 3.6 eV reported for this compound by Yim et al\cite{1}, however, our band gap values are in good agreement with results of\cite{33, 34}.

The effective mass of carriers is important for investigating the photocatalytic activity and transport properties of materials. In this work, the effective mass of electrons ($m_e^*$) in relation to the CB bottom and the holes effective mass ($m_h^*$) in relation to the VB top in ZnRE$_2$S$_4$ ($RE = Er, Tm$) compounds are obtained based on the energy-independent scattering approximation\cite{35, 36} given by equation (1):

$$m^* = \hbar^2 \left( \frac{\partial^2 E}{\partial^2 k} \right)^{-1}$$ \hspace{1cm} (1)

Considering data listed in Table 3, we can see that the charge carriers of the studied materials are quite light, whose effective mass is found at the order of $10^{-3}$ $m_0$ ($m_0 =$ free electron mass), except the electrons moving in the $\Gamma$–$Z$ direction. Undoubtedly, the very low effective masses are results of the highly dispersive curves. Furthermore, one can note a significant difference between two electrons effective masses $m_e^*$ caused by the high dispersive bands along the $\Gamma$–$X$ direction at CBM\text{a} with respect to the bands along the $\Gamma$–$Z$ direction (in the $k$-space) that are flat. On the contrary, a small difference between the two masses $m_h^*$ is observed due to somewhat isotropic dispersion along the $\Gamma$–$Z$ and $\Gamma$–$X$ directions (in the $k$-space) at CBM\text{a}.

To reach a basic understanding of the electronic structure, the total and partial densities of states (TDOS and PDOS, respectively) of ZnRE$_2$S$_4$ ($RE = Er, Tm$) compounds were calculated using the GGA-PBE approach. Following figure 3, we observe that the low energy region of the valence band is composed mainly by 3$s$,3$p$ states of the sulfur (S) atoms mixed with 3$d$ states of the zinc (Zn) atoms for both materials. Moreover, the sharp peak

|                      | ZnEr$_2$S$_4$ | ZnTm$_2$S$_4$ |
|----------------------|---------------|---------------|
| $m_e^*$ $\Gamma$–$Z$ | $5.33 \times 10^{-2}$ | $4.7 \times 10^{-2}$ |
| $m_e^*$ $\Gamma$–$X$ | $7.7 \times 10^{-3}$ | $7.6 \times 10^{-3}$ |
| $m_h^*$ $\Gamma$–$Z$ | $1.36 \times 10^{-2}$ | $1.36 \times 10^{-2}$ |
| $m_h^*$ $\Gamma$–$X$ | $1.27 \times 10^{-2}$ | $1.23 \times 10^{-2}$ |

Figure 3. Total and partial projected densities of states of ZnRE$_2$S$_4$ ($RE = Er, Tm$) compounds.
positioned at the energy of $-4.4$ eV is formed essentially by the mixture of Zn 4$s$ and S 3$p$ states. Whereas, the upper valance band is dominated by the hybridization between S 3$p$ and Er/Tm 4$d$ states with small contributions of Er/Tm 6$s$, 5$p$ states and Zn 3$p$ states. The hybridization between S 3$p$ and Er/Tm 4$d$ states suggests mainly a covalent character of Er/Tm–S bonds. On the other hand, the conduction band (CB) displays sharp peaks originating mainly by the unfilled Er/Tm 4$d$ states with a small contribution of S 3$p$ states. One can also observe that both the valence band maximum and the conduction band minimum are essentially dominated by the mixture of electronic states associated with the (Er, Tm) atoms and sulfur atoms, suggesting that somewhat decreasing the bandgap value when going from ZnEr$_2$S$_4$ to ZnTm$_2$S$_4$ is caused by the small difference in the electronegativity of the lanthanide atoms.

3.3. Optical properties

Optical spectroscopy of solids is one of the most powerful phenomena for understanding the electronic structure of materials. In the dynamic field case, the optical spectroscopy can be described by the following dielectric complex function [37–39]:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$

where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts, respectively. In present work, we estimate the dielectric complex function and the optical properties of ZnRE$_2$S$_4$ (RE = Er, Tm) for incident radiation in the photon energy range from 0 eV up to 20 eV. Regarding the crystal symmetry of the herein studying materials, all-optical spectra were plotted along the main crystal directions $xx$, $yy$, and $zz$. We notice here a great similarity between the optical spectra of these materials that can be explained by the small difference in their energy bandgap values as well as some resemblance of filling the VB and CB regions by main contributors of the electronic states in the ternary sulfides under consideration.

Figure 4 presents the calculated $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ spectra as a function of the photon energy. Following figures 4(a), (b), we can determine the statical dielectric constants of ZnEr$_2$S$_4$ (ZnTm$_2$S$_4$) at zero photon energy ($h\nu = 0$) which are as follows: $\varepsilon_1^{xx} = 6.53$ (6.52), $\varepsilon_1^{yy} = 6.61$ (6.59) and $\varepsilon_1^{zz} = 6.56$ (6.56). In addition, the $\varepsilon_1(\omega)$ spectrum reveals main peaks in the extreme visible light region at approximately 3.3 eV and 3.4 eV for ZnEr$_2$S$_4$ and ZnTm$_2$S$_4$, respectively. With further increasing photon energy, the $\varepsilon_1(\omega)$ curves diminish rapidly until they yield negative values in the ultraviolet region caused by the electromagnetic ray damping, and, then, they increase gradually toward zero at an energy of about 17.15 eV, 17.3 eV and 17.78 eV along the $xx$, $yy$, and $zz$
direction, respectively. We notice here a clear anisotropy of the real part $\varepsilon_1(\omega)$ of the dielectric function in the UV region for both compounds caused by the different electron polarizability in the $x$-, $y$- and $z$- directions.

Besides, from figure 4, we can observe that the imaginary part of the dielectric function presents the existence of seven principal peaks A ($\sim 3.99$ eV), B ($\sim 4.11$ eV), C ($\sim 4.36$ eV), D ($\sim 4.74$ eV), E ($\sim 5.30$ eV), F ($\sim 6.42$ eV) and G ($\sim 6.86$ eV) which are directly associated to the absorption of photons provoked by the electrons transfer from the filled VB to the bottom of the unoccupied CB. The first five peaks (A, B, C, D, and E) correspond principally to transitions from $S_p$ and Er/Tm $d$ states to Er/Tm $d$ and Zn $s$ states, while F and G peaks are related essentially to transitions from $S_s$, $p$ and Zn $s$, $d$ states to Er/Tm $d$ states. It is worth noting that the interpretation about the origin of these peaks can correspond also to other existing transitions between the occupied and the unoccupied energy bands. The $\varepsilon_2(\omega)$ curves of ZnRE$_2$S$_4$ (RE = Er, Tm) compounds yield a remarkable anisotropy especially in the energy range between 3.5 eV and 12 eV.

Following the calculated $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ curves of the complex dielectric function, one can determine other optical coefficients such as optical reflectance $R(\omega)$, absorption $\alpha(\omega)$ and refraction $n(\omega)$ indices can be calculated based on the matrix value of the dielectric function [38, 39].

Figures 5(a), (b) illustrate the reflectivity $R(\omega)$, which correspond to the reflected electromagnetic energy percentage at the surface of a solid. At zero photon energy the $R(\omega)$ function of ZnEr$_2$S$_4$ (ZnTm$_2$S$_4$) are about of 19.16% (19.13%), 19.35% (19.32%) and 19.23% (19.23%) along $xx$, $yy$ and $zz$ direction, respectively. After that, the $R(\omega)$ spectra of both compounds increase with increasing photon energy and achieve their maxima at an

---

**Figure 5.** Dependence on photon energy of (a, b) the reflectivity $R(\omega)$, (c, d) absorption coefficient $\alpha(\omega)$, and (e, f) refractive index $n(\omega)$ of ZnRE$_2$S$_4$ (RE = Er, Tm).
energy level of 7–9.5 eV, which corresponds to negative values of $\varepsilon_1(\omega)$. The calculated absorption coefficient $\alpha(\omega)$ is illustrated in figure 5(c, d). This coefficient provides the fraction of energy lost by the incident radiation per length unit when it passes through a material. The absorption $\alpha(\omega)$ curves start to increase when the photon energy is higher than the absorption edge, in fact, in the visible light region. After that, the $\alpha(\omega)$ curves yield maximum values in the UV region for both compounds. Consequently, the strong absorption from the visible light to the UV region reveals that ZnEr$_2$S$_4$ and ZnTm$_2$S$_4$ are good absorbers overall the direct bandgap of 2.37 eV and 2.35 eV, respectively.

Following figure 5(e, f) representing the dependence of the refractive index $n(\omega)$ on photon energy, the $n(\omega)$ function of ZnEr$_2$S$_4$ (ZnTm$_2$S$_4$) enhances from its static values of about $n_{xx}(0) = 2.557$ ($2.554$), $n_{yy}(0) = 2.57$ ($2.568$) and $n_{zz}(0) = 2.562$ ($2.562$) at zero frequency to reach its highest values at photon energy around 3.5 eV. After that, the $n(\omega)$ spectra of both materials decrease with increasing photon energy and achieve their minima in the UV region.

We notice here a clear anisotropy of the optical coefficient in the UV region for ZnRE$_2$S$_4$ (RE = Er, Tm) compounds. Moreover, since the structural symmetry and anisotropic refractive index ($n^{xx} \neq n^{yy} \neq n^{zz}$) of ZnEr$_2$S$_4$ and ZnTm$_2$S$_4$ may have more than one axis of anisotropy, consequently these materials exhibit biaxial birefringence or trirefringence. The evaluated birefringences, $\Delta n(\omega)$, for the studied compounds along the three axes, using the calculated refractive indices, are illustrated in figure 6. From this figure, one can observe the similarity of the $\Delta n$ curves of both materials. Besides, the $\Delta n$ curves are almost constant in the non-absorbing region, i.e. under the energy gap, and show strong oscillation above this region. The values of the trirefringence at zero energy of ZnRE$_2$S$_4$ (RE = Er, Tm) compounds are reported in Table 4. We observe that the value of $\Delta n^{zx}$ at zero energy is larger than other ones for both compounds that represent the magnitude of the birefringence of the sections, $\Delta n_{s}$ [40].

### Table 4. The values of the biaxial birefringence $\Delta n$ at zero energy.

| Material    | $\Delta n^{xx}$ | $\Delta n^{yy}$ | $\Delta n^{zz}$ |
|-------------|-----------------|-----------------|-----------------|
| ZnEr$_2$S$_4$ | 0.0140          | 0.0052          | −0.0087         |
| ZnTm$_2$S$_4$ | 0.0139          | 0.0074          | 0.0065          |

### 3.4. Elastic properties

It is well known that the response of solid to the externally applied forces can generally be determined through the elastic constants $C_{ij}$, and their quantities can also give important information on the strength and stiffness of materials, chemical bonding character, thermal properties and so on. In the present work, the nine elastic constants $C_{111}, C_{122}, C_{133}, C_{222}, C_{233}, C_{444}, C_{555}$, and $C_{66}$ for orthorhombic ZnRE$_2$S$_4$ (RE = Er, Tm) compounds were estimated by calculating the change in total energy against applied strain to the equilibrium volume (see Table 5). In addition, the mechanical stability of the structure is assured only if the strain energy is positive when any homogeneous elastic deformation is applied. In the case of an orthorhombic system, this requires the following criteria to be realized [41]:

![Figure 6. The evaluated biaxial birefringence of ZnEr$_2$S$_4$ and ZnTm$_2$S$_4$.](image-url)
The fact that all the $C_{ij}$ constants are positive and obey these criteria indicates that both compounds, ZnEr$_2$S$_4$ and ZnTm$_2$S$_4$, are mechanically stable. Moreover, from data listed in Table 5, we can see that $C_{11} < C_{22} < C_{33}$ for both compounds; consequently the mechanical strength along [100] direction is weaker than that along [010] and [001] directions and the shearing strength at (001) plane is stronger in comparison with other planes, (100) and (010). We have also found the following relation for the elastic constants: $C_{66} < C_{55} < C_{44}$. This corresponds to the shear moduli for (001), (010) and (100) crystal planes, respectively.

Now using these elastic constants one can determine other mechanical parameters such as bulk modulus $B$, Young’s modulus $E$, shear modulus $G$, and Poisson coefficient $\nu$. Using Voigt-Reuss-Hill approximations [42–44] these mechanical parameters for the orthorhombic system are defined as:

$$B_V = \frac{1}{9}(C_{11} + C_{22} + C_{33}) + \frac{2}{9}(C_{12} + C_{13} + C_{23})$$

$$G_V = \frac{1}{15}(C_{11} + C_{22} + C_{33}) - \frac{1}{15}(C_{12} + C_{13} + C_{23}) + \frac{1}{5}(C_{44} + C_{55} + C_{66})$$

$$B_R = \frac{1}{(S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{13} + S_{23})}$$

$$G_R = \frac{1}{15}4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{13} + S_{23}) + 3(S_{44} + S_{55} + S_{66})$$

$$B_H = (B_V + B_R)/2$$

$$G_H = (G_V + G_R)/2$$

$$E = 9B_HG_H/(3B_H + G_H)$$

$$\nu = (3B_H - 2G_H)/[2(3B_H + G_H)]$$

where $C_{ij}$ is the elastic constants and $S_{ij}$ are the elastic compliances.

In view of the fact that information regarding strength and hardness of materials can be given by the values of the mechanical parameter (bulk modulus $B$, Young’s modulus $E$, shear modulus $G$) [45], the ZnRE$_2$S$_4$ compounds are expected to have weak hardness due to their low moduli. We noticed here that a strong relationship exists between Poison’s ratio and volume change during uniaxial deformation, hence for $\nu = 0.5$ there is no volume change throughout uniaxial deformation [46]. In the case of the compounds under study, $\nu < 0.5$, i.e. there is some volume change related to its elastic deformation. Moreover, information concerning the characteristics of the bonding forces of compounds can be provided via Poison’s ratio [47], so the value of $\nu = 0.25$ is considered as the lower bond for central force of solids, whereas $\nu = 0.5$ is the upper one, which represents the infinite elastic anisotropy of solids [48]. From Table 6, we see that $0.25 < \nu < 0.5$; this means that

Table 5. Calculated values (in GPa) of elastic constants $C_{11}$, $C_{12}$, $C_{13}$, $C_{22}$, $C_{23}$, $C_{33}$, $C_{44}$, $C_{55}$, $C_{66}$ of ZnRE$_2$S$_4$ (RE = Er, Tm) crystals.

|         | $C_{11}$  | $C_{12}$  | $C_{13}$  | $C_{22}$  | $C_{23}$  | $C_{33}$  | $C_{44}$  | $C_{55}$  | $C_{66}$  |
|---------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| ZnEr$_2$S$_4$ | 100.52    | 41.64     | 47.06     | 107.33    | 48.11     | 118.19    | 36.57     | 34.29     | 28.83     |
| ZnTm$_2$S$_4$ | 103.06    | 41.20     | 50.57     | 108.98    | 49.63     | 123.03    | 36.45     | 34.97     | 28.09     |

Table 6. Estimated values (in GPa) within Voigt-Reuss-Hill’s approximation of the bulk modulus ($B$), shear modulus ($G$), Young’s modulus ($E$) and Poisson’s ratio $\nu$, $B/G$ and shear anisotropic factors ($A_1$, $A_2$, and $A_3$) of ZnRE$_2$S$_4$ (RE = Er, Tm) crystals.

|         | $B_V$    | $B_R$    | $B_H$    | $G_V$    | $G_R$    | $G_H$    | $E$     | $\nu$    | $A_1$    | $A_2$    | $A_3$    |
|---------|----------|----------|----------|----------|----------|----------|---------|----------|----------|----------|----------|
| ZnEr$_2$S$_4$ | 66.70    | 66.15    | 66.42    | 32.53    | 32.26    | 32.39    |        |          |          |          |          |
| ZnTm$_2$S$_4$ | 68.63    | 67.83    | 68.23    | 32.82    | 32.46    | 32.64    |        |          |          |          |          |
| ZnEr$_2$S$_4$ | 2.05     | 83.58    | 0.290    | 1.13     | 1.09     | 1.01     |        |          |          |          |          |
| ZnTm$_2$S$_4$ | 2.09     | 84.45    | 0.293    | 1.09     | 1.11     | 0.95     |        |          |          |          |          |

\[ C_{11} > 0, C_{22} > 0, C_{44} > 0, C_{55} > 0, C_{66} > 0; \]
\[ [C_{11} + C_{33} + C_{22} + 2(C_{44} + C_{13} + C_{23})] > 0; (C_{11} + C_{22} - 2C_{12}) > 0; \]
\[ (C_{11} + C_{33} - 2C_{33}) > 0; (C_{22} + C_{33} - 2C_{23}) > 0 \]
the interatomic forces in the ZnRE$_2$S$_4$ compounds are somewhat central. Besides, Pugh [49] has proposed an empirical ratio ($B/G$) linked between the plastic properties of the material and their elastic moduli, which predict the brittleness ($B/G < 1.75$) and ductility ($B/G > 1.75$) of materials. From Table 6, it is clear that our values of $B/G$ ration are higher than 1.75 for both compounds, suggesting a ductile behavior of ZnRE$_2$S$_4$ (RE = Er, Tm) materials and, therefore, they will be resistant to thermal shocks.

The calculation of the elastic anisotropy for solids plays a major key to understand the mechanical behavior of the materials since it is well known that the elastic anisotropy is responsible for microcracks in solids [50]. The shear anisotropic factor is recognized as one of the most factors which quantify the degree of anisotropy in atomics bonding in different planes. This factor is defined for the (100) shear planes between the [101] and [010] directions as:

$$A_1 = 4C_{44}/(C_{22} + C_{33} - 2C_{32})$$  \hspace{2cm} (12)

for the (010) shear planes between [011] and [001] directions as:

$$A_2 = 4C_{55}/(C_{11} + C_{33} - 2C_{13})$$  \hspace{2cm} (13)

and for the (001) shear planes between [110] and [010] directions as:

$$A_3 = 4C_{66}/(C_{11} + C_{22} - 2C_{12})$$  \hspace{2cm} (14)

For an isotropic crystal the factors $A_1$, $A_2$, and $A_3$ must be equal to unity, while any value smaller or greater than one is a measure of the elastic anisotropy degree possessed by the crystal. These factors are presented in Table 6. From this table we observed that $A_3$ presents the smallest deviation from the unity at about 0.01 and 0.05.
for ZnEr$_2$S$_4$ and ZnTm$_2$S$_4$, respectively, indicating that the shear anisotropic factors for the (001) shear plane are more isotropic than $A_1$ and $A_2$.

Now, to well quantify the anisotropic degree in these materials, the directional dependences of the linear compressibility ($1/B$) and Young’s modulus ($E$) are visualized in the 3D and 2D forms (figures 7 and 8) using ELATE [51]. From figure 7(a), we can observe that the linear compressibility plots present a quasi-spherical profile indicating some directionality of the compressibility for ZnEr$_2$S$_4$ and ZnTm$_2$S$_4$. This can be well found from the projections of the linear compressibility in the $xy-$, $xz-$, and $yz-$ planes figure 7(b). In the $xy-$ plane, the linear compressibility is somewhat isotropic, whereas anisotropy in $xz-$ or $yz-$ planes is revealed. This result implies that both materials are weaker against compression in the $xz-$ or $yz-$ planes. On the other hand, higher anisotropy is observed from Young’s modulus plots when a deviation from the spherical form is noticeable (figure 8(a)). Moreover, the projections of Young’s moduli in the $yz-$, $xz-$ and $xy-$ planes (figure 8(b)) reveal higher anisotropy in the $xy-$ plane than that in the $xz-$ or $yz-$ planes. This significant difference suggests strong resistance of ZnEr$_2$S$_4$ and ZnTm$_2$S$_4$ to the uniaxial stress along [001] direction.

Figure 8. Three-dimensional (3D) curved surface representations of (a) Young’s modulus $E$ and (b) its projections along three different planes for ZnEr$_2$S$_4$ and ZnTm$_2$S$_4$.
4. Conclusion

In this study, we have investigated electronic, optical and mechanical anisotropy of ZnRE$_2$S$_4$ (RE = Er, Tm) olivine compounds within PP-PAW method. The calculated unit cell parameters are in good agreement with the experimental ones. In addition, the study of electronic properties reveals that ZnEr$_2$S$_4$ and ZnTm$_2$S$_4$ are semiconductors with a direct bandgap of about 2.37 eV and 2.35 eV, respectively. Besides, the presence of flat and dispersive bands at the conduction band minimum of the studied compounds is responsible for the significant difference between two electrons effective masses, along Γ–Z and Γ–X directions, an indicator of anisotropic effect on $m_x$. From the analyzed optical constants, we observe a clear anisotropy of these constants in the UV region for both compounds caused by the different electron polarizability along the $x$–, $y$– and $z$– directions. Moreover, both materials are transparent in the IR region and yield strong absorption in the visible region for both compounds. Furthermore, the elastic constants are estimated allowing to state that ZnEr$_2$S$_4$ and ZnTm$_2$S$_4$ compounds are mechanically stable and reveal ductility behavior. The calculation of the elastic anisotropy implies that both materials are weaker against compression in the $m_x$, $m_y$, and $m_z$ directions. Moreover, both materials are transparent in the IR region and yield strong absorption in the visible region. Finally, we expect that the present investigation will be helpful for further experimental findings and probable practical applications of these olivine semiconductors.

Acknowledgments

This research is funded by the Vietnam National Foundation for Science and Technology Development (NAFOSTED) under Grant Number 103.01/2018.334.

ORCID iDs

T Seddik https://orcid.org/0000-0002-4623-107X
Tuan V Vu https://orcid.org/0000-0003-3872-8323

References

[1] Yim W M, Fan A K and Stolfo E J 1973 J. Electrochem. Soc. 120 441
[2] Aliev O M, Agaev A B and Azadaliyev R A 1997 Inorg. Mater. (Transl. of Neorg. Mater.) 33 1123–7
[3] Schewe V and White W B 1983 Mat. Res. Bull. 18 1059–68
[4] Reshak A H 2017 J. Alloy. Compd. 728 241–52
[5] Batoouche M et al 2019 Physica B 558 91–9
[6] Koenig J 1985 Thermal and Mechanical Properties of Calcium Lanthanum Sulfide (Birmingham, AL: Southern Research Institute)
[7] Steinfink H and Swine J S 1987 Mat. Res. Soc. Symp. Proc. 97 371–8
[8] Agaev A B, Rustamov P G, Agaev O M and Azadaliyev R A 1989 Inorg. Mater. (Transl. of Neorg. Mater.) 25 250–4
[9] Batoouche M, Belfarh T, Si Mohamed D E, Tabeti A, Seddik T, Ug ur S, Ug ur G and Belfedal A 2018 Physica B 545 40–7
[10] Heikens H H, Kuindersma R S, Van Bruggen C F and Haas C 1978 Phys. Stat. Sol. A 46 687–95
[11] Tomas A, Shilo I and Guittard M 1978 Mater. Res. Bull. 13 857
[12] Pawlak L, Falkowski K and Pokrzywnicki S 1981 J. Solid State Chem. 37 238
[13] Tomas A, Guittard M, Flahaut J, Guymont M, Portier R and Gratias D 1986 Acta Cryst. B 42 364
[14] Pawlak L and Duzznal M 1992 Alloy. Compd. 184 203–9
[15] Lau G C, Freitas R B, Schiffer P and Cava R J 2006 Phys. Rev. B 72 054411
[16] Lago J, Zvickovic I, Malik B Z, Rodriguez-Fernandez J, Ghigna P, Dalmas de Rotetier P, Yaounac A and Rojo T 2010 Phys. Rev. Lett. 104 247203
[17] Hatrafi J, Merabiha O, Seddik T, Baltache H, Khnata R, Ahmed R, Khan S A, Bouhemadou A, Azam S and Bin- Omran S 2017 Bull. Mater. Sci. 40 105–10
[18] Hills M E 1989 Preparation, Properties, and Development of Calcium Lanthanum Sulfide as an 8– to 12-micrometer Transmitting Ceramic (China Lake, CA: Naval Weapons Center).
[19] Sawant R R, Shinde S S, Bhosale C H and Raipure K Y 2010 Sol. Energy 84 1208
[20] Zhang W, Yang H, Fu W, Li M, Li Y and Yu W 2013 J. Alloy. Compd. 561 10–5
[21] Reshak A H 2018 Phys. Chem. Chem. Phys. 20 8848
[22] Vollebregt F H A and Ido D W 1982 Acta Cryst. B 38 2442
[23] Blochl P E 1994 Phys. Rev. B 50 17953
[24] Kresse G and Joubert D 1999 Phys. Rev. B 59 1758
[25] Kresse G and Hafner J 1993 Phys. Rev. B 48 13115
[26] Kresse G and Furthmuller J 1996 Phys. Rev. B 54 11169
[27] Perdew J P, Burke K and Ernzerhof M 1997 Phys. Rev. Lett. 78 1396
[28] Monkhorst H J and Pack J D 1976 Phys. Rev. B 13 5188
[29] Page Y L and Saxe P 2002 Phys. Rev. B 65 104104
[30] Vincent H, Bertaut E F, Baur W H and Shannon R D 1976 Acta Crystallogr. B. Struct. Crystallogr. Cryst. Chem. 32 1749–55
[31] Mitchell K and Ibers J A 2002 Chem. Rev. 102 1929–52
[32] Momma K and Izumi F 2011 J. Appl. Crystallogr. 44 1272–6
[33] https://materialsproject.org/materials/mp-1192811/
[34] https://materialsproject.org/materials/mp-17043/
[35] Snyder G J and Toberer E S 2008 Nat. Mat. 7 105–14
[36] Cutler M, Leavy J F and Fitzpatrick R L 1964 Phys. Rev. 133 A1143–52
[37] Wooten F 1972 Optical Properties of Solids (New York: Academic)
[38] Vu T V, Lavrentyev A A, Gabrelian B V, Parasyuk O V, Ocheretova V A and Khyzhun O Y 2018 J. Alloy. Compd. 732 372–84
[39] Ambrosch-Draxl C and Sofis O 2006 Comput. Phys. Commun. 175 1–14
[40] Baeed J, Hosseini S M, Kompany A and AttaranKahki E 2008 Phys. Stat. Sol. (b) 245 2572–80
[41] Wallace D C 1972 Thermodynamics of Crystals (New York: Wiley)
[42] Voigt W 1928 Lehrbuch der Kristallphysik (Leipzig und Berlin: Verlag und Druck, Von BG Teubner)
[43] Reuss A 1929 Z. Angew. Math. Mech. 9 49
[44] Hill R 1952 Proc. Phys. Soc. 65 349
[45] Frantsevich I N, Voronov F F and Bokuta S A 1983 Elastic Constants and Elastic Moduli of Metals and Insulators (Kiev: Naukova Dumka) 60–180
[46] Ravindran P, Fast L, Korzhavyi P A and Johansson B 1998 J. Appl. Phys. 84 4891
[47] Köster W and Franz H 1961 Metall. Rev. 6 1–56
[48] Ledbetter M H 1983 Elastic properties Materials at Low Temperatures ed R P Reed and A F Clark (Metals Park, OH: American Society for Metals) ch. 1
[49] Pugh S F 1954 Philos. Mag. 45 823
[50] Seddik T et al 2017 Superlattices Microstruct. 109 1–12
[51] Gaillac R, Pullumbi P and Coudert F-X 2016 J. Phys. Condens. Matter 28 275201