Electronic, optical, elastic, thermoelectric and thermodynamic properties of the spinel oxides ZnRh$_2$O$_4$ and CdRh$_2$O$_4$

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A R T I C L E   I N F O

Article history:
Received 18 June 2018
Received in revised form 4 September 2018
Accepted 25 September 2018
Available online 29 September 2018

Keywords:
spinel oxides
First-principles calculations
Optoelectronic properties
Elastic constants
Thermoelectric parameters
Thermodynamic properties

A B S T R A C T

Density functional FP-LAPW+lo method calculations were performed to explore the structural, electronic, optical, elastic, thermoelectric and thermodynamic properties of the spinel oxides ZnRh$_2$O$_4$ and CdRh$_2$O$_4$. The exchange-correlation potential were described using the GGA-PBEsol and TB-mBJ functionals. As the first step, the optimized structural parameters, including the lattice parameter and atomic coordinates, were determined. Electronic band structure, atomic-resolved $l$-projected densities of electronic states and photon energy dependence of the linear optical functions were computed. It is found that both investigated compounds are indirect band gap semiconductors. The band gap results from the splitting of the Rh $: 4d^6$ states into occupied Rh $: 4d^t_{2g}$ states, which form the valence band maximum (VBM), and the empty states Rh $: 4d^c_{e^g}$, which form the conduction band minimum (CBM), owing to the octahedral substantial crystal-field. The electronic interband transitions responsible of the structures in the optical spectra were specified. Single-crystal and polycrystal elastic moduli, wave sound velocities, Debye temperature, Pugh’s indicator and indexes of elastic anisotropy were numerically estimated using total energy versus strain. FP-LAPW+lo band structure in combination with the standard Boltzmann transport theory were employed to calculate the thermoelectric parameters, including Seebeck coefficient, electrical and thermal conductivities and figure of merit. It is found that the title compounds are potential candidates for thermoelectric applications if one can further reduce their thermal conductivities via some techniques. FP-LAPW+lo approach in combination with the quasi-harmonic Debye model was employed to study temperature and pressure dependences of some macroscopic physical parameters. Our obtained results in the present work are discussed in comparison with the available experimental and theoretical data. The calculated results show a good agreement with the available experimental and theoretical results.

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1. Introduction

Transparent conducting oxides (TCOs) form an exceptional family of materials, possessing two important physical properties together: (i) high optical transparency to visible light and (ii) high electrical conductivity carrier concentrations [1]. Owing to these properties, the TCOs are technologically classified as an important class of materials in the field of optoelectronics [2]. TCOs have found a wide variety of technological applications, such as blue or ultraviolet light emitting diodes (LEDs), solar cells, flat-panel displays, liquid crystal displays, energy-conserving windows, smart windows, touch screens, light emitting displays, invisible security circuits, and dimming rear-view mirrors [2,3]. Most of the TCOs

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https://doi.org/10.1016/j.jallcom.2018.09.338
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possess n-type conductivity and the development of efficient p-
type TCOs is one of the main objectives of researchers. High-
conductivity p-type TCOs comparable with the high performance
n-type TCOs would be a major breakthrough, enabling advanced
devices and applications [4].

Spinel oxides have been identified as promising p-type trans-
parent conducting oxide semiconductors [5], which can be an
alternative to the n-type tin-doped indium oxide (commonly called
tin-indium-oxide or ITO) [2]. The perspectives of usage of the spinel
oxides as p-type transparent conducting oxide semiconductors and
for other applications have stimulated extensive experimental and
theoretical studies on this exciting class of materials [2,4–20].
Spinel oxides are characterized by their robust properties, such as
high melting temperature, high strength, high resistance to
chemical attack, large fundamental band gap and good electrical
conductivity [12].

The spinel oxides ZnRh2O4 and CdRh2O4 are promising trans-
parent semiconducting for various technological applications, such as
transparent “metallic” electrodes for solar cells and flat panel
displays, including liquid crystal displays (LCDs), and organic light-
emitting diodes (OLEDs) [7,15]. The perspectives of usage of the spinel
rhodates ZnRh2O4 and CdRh2O4 in the optoelectronics field
have been acted framework of some experimental and theoretical
researchers [2,4–11,14–17,20–22]. The spinel oxides ZnRh2O4 and
CdRh2O4 were synthesized and their crystalline structure identified
a long time ago [21,22]. Some of the fundamental physical prop-
erties of ZnRh2O4 and CdRh2O4, such as structural and electronic
properties, have been already investigated experimentally [4–11]
and theoretically via first-principles calculations [2,4,14–17,20].
However, some other fundamental properties, such as elastic
(ZnRh2O4), thermodynamic, optical (CdRh2O4) and transport
properties have not yet been addressed.

For optoelectronic applications, it is very necessary to accurately
determine the electronic and optical properties of the involved
materials. Therefore, the first objective of the present work is a
precise determination of the parameters characterizing the opto-
electronic properties of the title materials. For optoelectronic
applications, the involved materials are generally grown in form of
thin films on substrates. The lattice mismatch and difference in the
thermal expansion coefficients between the grown layers and
substrates could cause large stresses in the epitaxial layers, which
could affect their fundamental properties. Therefore, it becomes
requisite to evaluate their elastic constants, which characterize the
response of materials to applied stress. Thus, the second main
objective of the present work is a precise estimation of the elastic
constants and their related properties for the examined compo-
ounds. On the other hand, it is worthy to note that the reported
theoretical findings for ZnRh2O4 and CdRh2O4 [2,4,14–17,20]
were carried out only for the case of zero temperature, i.e.,
without including any thermal effect. Therefore, because of the not negli-
gible effects of temperature and pressure on the physical properties
of materials, the third main objective of the present work is an
estimation of temperature and pressure dependences of the lattice
parameter, bulk modulus, volume thermal expansion, isochoric
and isotropic heat capacities and Debye temperature of the title
compounds. Investigation of the thermoelectric performance of the
studied compounds constitutes the fourth objective of the present
study. Here, we carried out a first-principles study of some physical
properties of the spinel oxides ZnRh2O4 and CdRh2O4 using the full
potential linearized augmented plane wave plus local orbitals
method in the framework of density functional theory. Our results
cover the optimized structural parameters, electronic bands,
charge-carrier effective masses, total and partial densities of elec-
tronic states, photon energy dependence of the linear optical
functions, elastic moduli and their related properties, temperature
and pressure dependences of some macroscopic physical parame-
ters and thermoelectric performances of the ZnRh2O4 and CdRh2O4
compounds.

2. Computational details

All performed first-principles calculations in the present work
were carried out by means of the full potential linearized
augmented plane wave plus local orbitals (FP-LAPW+lo) method
[23] as implanted in the WIEN2k code [24]. In the FP-LAPW+lo
method, the wave functions are expanded in a linear combination
of radial atomic functions and their energy derivatives multiplied
by spherical harmonics inside non-overlapping spheres centered at
the atomic sites (called muffin-tin spheres; MTS) of radius RMT
and in plane wave basis set in the remaining space of the unit-cell
called (interstitial region; RI). The RMT were taken as large as
possible without overlap between the MTSs and to ensure that no
core–charge leakage out of the MTS. The wave functions in the IR
were expanded in a plane wave basis set with a cut-off parameter
\( R_{	ext{MT}} \) \( K_{\text{max}} \) equal to 9, where \( R_{	ext{MT}} \) is the smallest muffin-tin radius
and \( K_{\text{max}} \) is the maximum plane wave vector in the \( k \)-space.
The integration over the Brillouin zone was replaced by a summation
on a Monkhorst-Pack grid of \( 10 \times 10 \times 10 \) \( k \)-points [25]. The self-
consistent field iteration process was repeated until the calcu-
lated total energy of the crystal converged to less than \( 10^{-5}\text{Ry} \).
and the maximum force on any atom was smaller than 0.5 \( \text{mRy/\text{a.u.}} \)
atomic unit). For the structural, elastic and thermodynamic
properties, the electronic exchange-correlation (XC) effects were
described using the generalized gradient approximation (GGA) as
parameterized by Perdew et al. (the so-called GGA-PBEsol or
GGA08) [26]. For the electronic and optical properties, in addition
to the GGA08, we adopted the TB-mBJ (Tran-Blaha modified Beck-
Johnson) scheme to model the XC effects [27–29]. The TB-mBJ
approach is quite successful in reproducing the experimental
band gap [29–32].

The energy bands (\( E(k) \)) were extracted from the DFT calcula-
tions. The optical properties were calculated using the optical
package of the WIEN2k code. The imaginary part (\( \epsilon_2(\omega) \)) of the
dielectric function \( \epsilon(\omega) = \epsilon_1(\omega) + i \epsilon_2(\omega) \) was derived from
the first-principles calculations by summing over all contributions
of the direct electronic transitions from the occupied states in the
valence band to the unoccupied states in the conduction band; the
indirect and intraband transitions are ignored. The real part (\( \epsilon_1(\omega) \))
of the dielectric function was calculated from \( \epsilon_1(\omega) \) using the
Kramers-Kronig transformation. All-important linear optical func-
tions, including absorption coefficient \( a(\omega) \), refractive index \( n(\omega) \),
extinction coefficient \( k(\omega) \), reflectivity coefficient \( R(\omega) \) and elec-
tronic loss-energy function \( L(\omega) \), were calculated from \( \epsilon_1(\omega) \) and
\( \epsilon_2(\omega) \) using the well-established relationships [33].

Knowledge of the elastic constants \( C_{ij} \) of solids (both experi-
mentally and theoretically) is very important as the \( C_{ij} \) charac-
terize the response of solids to external stresses within the elastic
limit and are related to many fundamental physical properties
of solids. Therefore, it becomes of great importance to determine
the \( C_{ij} \) with accuracy. Accurate single-crystal elastic constants \( C_{ij} \) can
be obtained from first-principles calculations of the variation of
the unit cell total energy as a function of specific lattice distortions.
For a cubic system, three different distortions of the optimized unit
are required to calculate the three independent elastic constants:
\( C_{11}, C_{12} \) and \( C_{44} \). To check the reliability of the numerical
estimation of the \( C_{ij} \) for the considered compounds, two different sets
of deformations were applied to the ground state unit cell. Theoretical
details of these two different sets of distortion patterns to calculate
the \( C_{ij} \), which were developed by Chapin and Morteza, are given in
Transport properties of the considered compounds were calculated using Boltzmann’s transport theory within the constant scattering time approximation (CSTA) and the rigid band approximation (RBA) as implemented in the BoltzTraP program [34,35] to shed some light on their thermoelectric performance. A dense k-mesh of 50 × 50 × 50 k-points in the Brillouin zone was used to calculate the optical, density of states and thermoelectric properties.

3. Results and discussion

3.1. Structural properties

The spinel oxides ARh2O4 (A = Zn, Cd) crystallize in a face centered cubic lattice with the Fd3m (n. 227) space group symmetry. A unit cell of ZnRh2O4 is depicted in Fig. 1. The ARh2O4 unit cell contains 56 atoms or eight unit formulas (8 ARh2O4). There are eight A (A = Zn, Cd) cations, 16 Rh cations and 32 O anions in the unit cell, which are located at the Wyckoff positions: 8u (1/8, 1/8, 1/8), tetrahedra sites, 16d (1/2, 1/2, 1/2), octahedral sites, and 32e (u, u, u), respectively. Every atom A (A = Zn, Cd) is surrounded by four O atoms, forming a regular tetrahedron and every atom Rh is surrounded by six O atoms, forming a regular octahedron. The RhO6 octahedron and AO4 tetrahedron are connected to each other through common edges. The ARh2O4 compounds are characterized by two free structural parameters that are not fixed by the symmetry: (i) the lattice parameter (a) and (ii) the internal coordinate u, which governs the O atom position. At the first step in the present work, full structural optimizations of the considered compounds were performed to determine their equilibrium structural parameters, including the lattice parameter (a) and the internal coordinate (u). To do that, total energy was calculated for a series of primitive cell volumes, where the atomic positions were allowed to relax for each volume. The resulting total energy-volume curve was fitted to the Birch-Murnaghan equation of state [36] to determine the equilibrium primitive cell volume, bulk modulus B and its pressure derive B’. The optimized structural parameters using the GGA08, GGA96 [37] and LDA [38] are listed in Table 1 along with the available experimental and theoretical data. From Table 1, one appreciates the remarkably excellent agreement between the GGA08 optimized lattice parameter value and the corresponding experimental one. The relative deviation (d(%) ) of the calculated lattice parameter (a_{optimized}) from the measured (a_{measured}) one, defined as: d(%) = \left( \frac{a_{optimized} - a_{measured}}{a_{measured}} \right) \times 100), is less than 0.7% (0.4%) in the case of ZnRh2O4 (CdRh2O4). All investigated properties were calculated at the optimized structural parameters obtained via the GGA08. One can note that the lattice parameter of ARh2O4 increases as we go from Zn to Cd due to the increase of the ionic radii.

3.2. Electronic properties

The computed electronic energy band dispersions for the optimized crystal structures of the title compounds along the selected high-symmetry lines within the BZ using the GGA08 and TB-mBJ are depicted in Fig. 2. As it can be seen from Fig. 2, both studied spinels are indirect band gap semiconductors, where the valence band maximum (VBM) is located at the X point in the BZ while the conduction band minimum (CBM) is located near the X point along the X→Γ line. The main features (band dispersions) of the GGA08 and TB-mBJ band structures are practically the same, except that the TB-mBJ band gap is much larger than the GGA08 one. The GGA08 band gap sizes for ZnRh2O4 and CdRh2O4 are 0.87 eV and 0.81 eV, respectively. The GGA08 band gap for ZnRh2O4 is severely underestimated compared to the measured one, which ranges from 2.0 eV to 2.74 eV [4−7,9]. Experimental band gap for CdRh2O4 is not yet available. The TB-mBJ band gaps of ZnRh2O4 and CdRh2O4 are 2.54 eV and 2.48 eV, respectively. One appreciates that the TB-mBJ potential improves significantly the opening of the band gap. The calculated fundamental band gap of ZnRh2O4 using the TB-mBJ potential, which is 2.54 eV, compares very well with the available experimental values, which range from 2.0 eV to 2.74 eV [4−7,9]. Thus, one can state that TB-mBJ provides a reliable simple method that can be a viable alternative to the computationally expensive approaches for the calculation of band gaps with an acceptable accuracy. It is worthy to note that the discrepancy between

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**Table 1**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Present</th>
<th>Expt.</th>
<th>Others</th>
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<td></td>
<td></td>
</tr>
<tr>
<td>a&lt;sub&gt;0&lt;/sub&gt; 8.5038&lt;sup&gt;a&lt;/sup&gt;</td>
<td>8.506&lt;sup&gt;a&lt;/sup&gt;</td>
<td>8.57&lt;sup&gt;a&lt;/sup&gt;</td>
<td>8.7700&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>u 0.26049&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.263&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.290&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.26829&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>B&lt;sub&gt;0&lt;/sub&gt; 197.88&lt;sup&gt;c&lt;/sup&gt;</td>
<td>198.19&lt;sup&gt;c&lt;/sup&gt;</td>
<td>186.89&lt;sup&gt;c&lt;/sup&gt;</td>
<td>206.13&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>B’ 5.13&lt;sup&gt;c&lt;/sup&gt;</td>
<td>4.97&lt;sup&gt;c&lt;/sup&gt;</td>
<td>4.94&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>CdRh2O4</td>
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<td></td>
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<td>a&lt;sub&gt;0&lt;/sub&gt; 8.4161&lt;sup&gt;c&lt;/sup&gt;</td>
<td>8.489&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>0.26851&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.2628&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>186.89&lt;sup&gt;c&lt;/sup&gt;</td>
<td>206.13&lt;sup&gt;c&lt;/sup&gt;</td>
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<tr>
<td>B’ 5.13&lt;sup&gt;c&lt;/sup&gt;</td>
<td>4.97&lt;sup&gt;c&lt;/sup&gt;</td>
<td>4.94&lt;sup&gt;c&lt;/sup&gt;</td>
<td>5.01&lt;sup&gt;c&lt;/sup&gt;</td>
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</table>

<sup>a</sup>Ref. [21]; <sup>b</sup>Ref. [9]; <sup>c</sup>Ref. [2]; <sup>d</sup>Ref. [17]; <sup>e</sup>Ref. [22]; <sup>f</sup>Ref. [11]; <sup>g</sup>Ref. [15]; <sup>h</sup>Ref. [16].
experimental data reported by different researcher groups for the ZnRh$_2$O$_4$ band gap is probably due to the experimental errors that usually arise from the used measurement technique and sample quality. In addition, this discrepancy between experimental data can be explained by the fact that the band gap value depends on the temperature at which the measurement is done. Our calculated band gaps using the GGA08 are consistent with the earlier reported theoretical results (Table 2) using the standard LDA and GGA methods [2,16]. Our TB-mBJ band gaps are also consistent with the earlier reported theoretical results using the TB-mBJ and hybrid functionals (sX-LDA) [15,16,20]. It might be worth mentioning that the minor differences between our TB-mBJ band gaps and the earlier reported results using TB-mBJ could be attributed to the fact that these values are derived from calculations performed at slightly different values of the equilibrium structural parameters; the band gap value is sensitive to the structural parameter values. One can note the downward trend of the fundamental band gap when moving from ZnRh$_2$O$_4$ to CdRh$_2$O$_4$ in accordance with the electronegativity trend.

Qualitative information about the ability of the studied compounds to easily conduct electricity can be obtained from the analysis of the energy band dispersions at the energy band extremes. Fig. 2 shows that the valence bands around the VBM

Fig. 2. Calculated band structures for ZnRh$_2$O$_4$ and CdRh$_2$O$_4$ using the GGA08 and TB-mBJ. The Fermi level is set to zero energy. Conduction-band minimum occurs near X-point along the X-G direction in the BZ.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Present</th>
<th>Using GGA08</th>
<th>Using TB-mBJ</th>
<th>Expt.</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnRh$_2$O$_4$</td>
<td></td>
<td>0.85</td>
<td>2.54</td>
<td>2.0–2.74</td>
<td>2.087 [15], 2.509 [16], 2.623 [15]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.53 [20], 2.88 [20], 3.33 [2]</td>
<td>0.897 [16], 1.65 [4]</td>
</tr>
<tr>
<td>CdRh$_2$O$_4$</td>
<td>Present</td>
<td>0.74</td>
<td>2.48</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.065 [15], 2.623 [15]</td>
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</table>
are less dispersive than the conduction bands around the CBM, which indicate that the effective mass of the hole will be heavier than that of the electron. This result suggests that the p-doped ZnRh2O4 and CdRh2O4 compounds should be more favourable for thermoelectric performance than the n-doped ones, while the electrical conductivity by conduction band electrons should be more favourable than that by valence band holes.

Transport properties in semiconductors are principally controlled by the effective masses of charge-carriers. Therefore, it becomes necessary to evaluate the electron and hole effective masses of the investigated compounds at the band edges. To calculate the hole effective mass \( m_h^* \) (electron effective mass \( m_e^* \)), we first fit the dispersion \( E(k) \) of the topmost valence band (lowest conduction band) around the VBM (around the CBM) to a quadratic polynomial in the reciprocal lattice vector \( k \):

\[
E(k) = A k^2,
\]

then the effective mass \( m^* \) (in unit of \( m_0 \), where \( m_0 \) denotes the electron rest mass) can be estimated using the following expression:

\[
\frac{1}{m^*} = \frac{m_0^2}{4} \left( \frac{\partial E}{\partial k} \right)^2 |_{k=k_0}.
\]

Predicted effective masses \( m_h^* \) at the VBM and \( m_e^* \) at the CBM towards the \( \Gamma \) directions for ZnRh2O4 and CdRh2O4 are listed in Table 3. It is apparent that both \( m_h^* \) and \( m_e^* \) exhibit a noticeable dependence on the crystallographic directions. The values of \( m_h^* \) and \( m_e^* \) towards the \( \Gamma \) direction are larger than the corresponding ones towards the \( \Gamma \) direction, suggesting that the mobility of the charge-carriers along the \( \Gamma \) direction should be larger than that along the \( \Gamma \) direction. The obtained results show also that the effective mass of the hole in ZnRh2O4 is more dependent on the crystallographic directions than that of the electron. Hence, the electrical conductivity by holes should be more anisotropic than that by electrons. In addition, the hole effective mass is larger than the electron one, indicating that the hole mobility should be smaller than the electron one in the considered compounds. Therefore, as the electrical conductivity \( \sigma \) is inversely proportional to the charge-carrier mass, one can expect that for the same charge-carrier concentration and temperature, the electrical conductivity \( \sigma \) of the n-type doped system should be larger than that of the p-type doped one. Moreover, as the Seebeck coefficient \( S \) is proportional to the effective mass of charge-carrier, one can expect that the \( S \) of the p-type doped system should be larger than that of the n-type doped one.

A closer examination of the electronic structure can be obtained by calculating the total density of states TDOS (states/eV/unit-cell) and atomic-resolved l-projected density of states PDOS (states/eV/atom/orbital) diagrams. The TDOS and PDOS spectra of the title compounds are illustrated in Fig. 3. The valence bands can be divided into three distinct groups (four groups) for ZnRh2O4 (CdRh2O4): V1, V2 and V3 (V1, V2, V3 and V4). For both studied spinels, the lowest energy valence band group (not shown in Fig. 3 for seek of clarity), ranging from approximately -0.8 eV to -19.6 eV, arises from the O: 2s orbitals. The V2 valence band group in the TDOS spectrum of ZnRh2O4, extending from approximately -7.7 eV to -2.1 eV, is originated mainly from the Zn:

Table 3
Calculated electron and hole effective masses at the CBM and VBM, respectively, towards the X→W and X→Γ directions in the Brillouin zone.

<table>
<thead>
<tr>
<th></th>
<th>ZnRh2O4</th>
<th>CdRh2O4</th>
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<tbody>
<tr>
<td></td>
<td>( m_h^* )</td>
<td>( m_h^* )</td>
</tr>
<tr>
<td>X→W</td>
<td>0.652</td>
<td>0.604</td>
</tr>
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</table>

Fig. 3. Calculated total and partial densities of states (TDOS and PDOS) for ZnRh2O4 and CdRh2O4. The Fermi level is set to zero. p.c.: primitive cell.
3d and O: 2p orbitals. For the CdRh$_2$O$_4$ case, the V3 group, ranging from approximately −8.3 eV to −7.4 eV, consists of the 4d and O: 2p states and the V2, ranging approximately from −8.3 to −7.4 eV, is composed of an admixture of the Rh: 4d and O: 2s orbitals. The upper valence band group, ranging from approximately −1.8 eV to Fermi level for ZnRh$_2$O$_4$ and from approximately −1.5 eV to Fermi level for CdRh$_2$O$_4$, is formed from the strongly hybridized occupied Rh: 4d − t$_{2g}^0$ and O: 2p states, suggesting a directional covalent bond between the Rh and O atoms. The lowest energy conduction band group (C1) is dominated by the unoccupied Rh: 4d − e$_g^0$ with significant contribution from the O: 2p states. The Rh: 4d$^6$ states are separated into occupied Rh: 4d − t$_{2g}^0$ states, which form the VBM, and empty Rh: 4d − e$_g^0$ states, which form the CBM, owing to the octahedral crystal-field splitting [4].

3.3. Optical properties

Fig. 4 depicts the imaginary (ε$_2$(ω)) and real (ε$_1$(ω)) parts of the dielectric function (ε(ω)) of the considered compounds. The ε$_2$(ω) spectrum of each considered compound exhibits 10 critical point structures, labelled E$_1$, E$_2$,.. E$_{10}$ in the figure. The behavior of ε$_2$(ω) spectrum is rather similar for ZnRh$_2$O$_4$ and CdRh$_2$O$_4$ over the considered range of energy. It is worth to attempt to identify the electronic transitions that are responsible for the ε$_2$(ω) spectrum structures from the calculated band structures. To determine the microscopic origin of the observed peaks, the ε$_2$(ω) spectrum was decomposed into individual contributions from each direct allowed electronic transition from occupied valence state V$_i$ to the unoccupied conduction state C$_j$ (V$_i$→C$_j$). Fig. 5 shows the decomposition of the ε$_2$(ω) spectrum of ZnRh$_2$O$_4$ into band to band contributions and the dispersion of the transition energy bands E$_i$(k) = E$_C$(k) − E$_V$(k). The positions of the main peaks E$_i$ of the ε$_2$(ω) spectrum and the extended direct inter-band transitions that contribute dominantly to the optical structures and their locations in the Brillouin zone for ZnRh$_2$O$_4$ are given in Table 4. Based on the TDOS diagram of ZnRh$_2$O$_4$ (CdRh$_2$O$_4$), the main contributions to the ε$_2$(ω) spectrum are originated from the electronic direct transitions from the valence band groups V1 and V2 (V1, V2 and V3) to the conduction band group C1. Based on the PDOS spectrum of ZnRh$_2$O$_4$ (CdRh$_2$O$_4$), we can conclude that the optical structures E$_i$, E$_2$, E$_3$ and E$_4$ of the ZnRh$_2$O$_4$ (CdRh$_2$O$_4$) ε$_2$(ω) spectrum are originated mainly from the electronic direct transitions from the occupied Rh: 4d − t$_{2g}^0$ and the O: 2p (in a second degree) valence band states to the unoccupied Rh: 4d − e$_g^0$ and O: 2p conduction band states. The optical structures E$_5$, E$_6$, E$_7$, E$_8$, E$_9$ and E$_{10}$ are resulted from the electronic direct transitions from the Zn: 3d (or Cd: 4d) valence bands to the Rh: 4d − e$_g^0$ and O: 2p conduction band states.

The electronic part of the static dielectric constant ε(0), a parameter of fundamental importance in many aspect of materials science, can be obtained from the low energy limit of the ε$_1$(ω) spectrum, i.e., ε$_1$(ω→0). The calculated static dielectric constants for ZnRh$_2$O$_4$ and CdRh$_2$O$_4$ are respectively equal to 4.262 and 5.126. The ε$_1$(0) value of ZnRh$_2$O$_4$ is lower than that of CdRh$_2$O$_4$. This result is consistent with Penn model [39]: ε$_1$(0) ≈ 1 + (hω$_p$/E$_g$)$^2$, where hω$_p$ is the plasma energy, i.e., larger is the band gap smaller is the static dielectric constant ε$_1$(0).

Photon energy dependence of the optical complex refractive index n (n = n + ik), which is an interesting optical parameter for the design of optoelectronic devices, is presented in Fig. 6 for the two studied compounds. The calculated zero energy (hω$_0$ = 0, λ = ω) n(0) value for ZnRh$_2$O$_4$ (CdRh$_2$O$_4$) is equal to 2.065 (2.263). The n(ω) maximum value of ZnRh$_2$O$_4$ (CdRh$_2$O$_4$), which is equal to 3.105 (3.242), is produced for a photon energy of about 5.80 eV (−6.24 eV). The maximum value of the extinction coefficient k(ω), which is equal to 2.534 (2.168), appears for a photon energy of about 6.90 eV (−6.91 eV) for ZnRh$_2$O$_4$ (CdRh$_2$O$_4$).

The absorption coefficient α(ω), which gives the fraction of energy lost by the incident radiation per length unit when it passes through a material, is depicted in Fig. 6. The absorption coefficient α(ω) of ZnRh$_2$O$_4$ (CdRh$_2$O$_4$) starts to increase when the photon energy is higher than the absorption edge and reaches its maximal value ~1.77 × 10$^6$ cm$^{-1}$ (~1.53 × 10$^6$ cm$^{-1}$) at approximately 7 eV. This is a typical characteristic of semiconductors and insulators. ZnRh$_2$O$_4$ (CdRh$_2$O$_4$) exhibits a noticeable absorption (~10$^6$ cm$^{-1}$) in the energy range between 6 eV and 10 eV (6 eV and 8.5 eV).

![Fig. 4](image-url) Calculated real (ε$_1$(ω)) and imaginary (ε$_2$(ω)) parts of the dielectric function for ZnRh$_2$O$_4$ and CdRh$_2$O$_4$. The critical point structures (peaks) are point out by the label E$_i$ (i = 1 to 10).
Fig. 5. Decomposition of the imaginary part ($\varepsilon_2(\omega)$) of the dielectric function into band-to-band contributions (top panel) and the transition energy band structure (bottom panel) for the cubic spinel ZnRh$_2$O$_4$. The counting of the bands is down (up) from the top (bottom) of the valence (conduction) band.

Table 4
Peak positions of the $\varepsilon_2(\omega)$ spectrum together with the dominant interband transition contributions to every peak and their location in the Brillouin zone for ZnRh$_2$O$_4$. The counting of the bands is down (up) from the top (bottom) of the valence (conduction) band.

<table>
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<tr>
<th>Optical structures</th>
<th>Dominant interband transition contributions</th>
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<tbody>
<tr>
<td>Structure Peak position</td>
<td>Transition Region Percentage Energy (eV)</td>
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<td>$E_1$  2.96</td>
<td>(V$_1$-C$_1$) W-L, $\Gamma$-X-W-K 25% 2.92</td>
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<td>2</td>
<td>(V$_1$-C$_1$) W-L, $\Gamma$-X 19.5% 2.97</td>
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<td>(V$_1$-C$_1$) $\Gamma$-X-W 51% 2.82</td>
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<td></td>
<td>(V$_4$-C$_1$) $\Gamma$-X-W 9.8% 2.99</td>
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<tr>
<td>$E_2$  3.38</td>
<td>(V$_1$-C$_1$) $\Gamma$-X-W 12.33% 3.26</td>
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<tr>
<td>3.42</td>
<td>(V$_1$-C$_1$) $\Gamma$-X-W 17.49% 3.29</td>
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<tr>
<td></td>
<td>(V$_1$-C$_1$) W-L 6.98% 3.54</td>
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<tr>
<td></td>
<td>(V$_1$-C$_1$) W-L, $\Gamma$-X-W-K 15.16% 3.29</td>
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<td>(V$_2$-C$_1$) $\Gamma$-X-W 9.03% 3.17</td>
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<td>(V$_2$-C$_1$) W-L, $\Gamma$-X 3.11% 3.07</td>
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<td>(V$_3$-C$_1$) $\Gamma$-X-W-K 6.47% 3.34</td>
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<tr>
<td></td>
<td>(V$_3$-C$_2$) W-L, $\Gamma$-X-W-K 14.78% 3.04</td>
</tr>
<tr>
<td>$E_3$  3.77</td>
<td>(V$_1$-C$_5$) W-L, X-W-K 17.25% 3.61</td>
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<td>4.55</td>
<td>(V$_1$-C$_5$) W-L, W-K 29.23% 3.49</td>
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<td>(V$_3$-C$_5$) W-L, $\Gamma$-X-W-K 5.89% 3.74</td>
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<td>(V$_5$-C$_7$) L-$\Gamma$, $\Gamma$-X-W 5.82% 3.74</td>
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<td>(V$_5$-C$_8$) W-L, X-W-K 10.76% 3.79</td>
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<td>$E_4$  4.19</td>
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<td>4.27</td>
<td>(V$_3$-C$_1$) W-L, W-X 7.96% 4.16</td>
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<td>(V$_3$-C$_3$) W-L, $\Gamma$-X-W-K 5.31% 3.91</td>
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<td>(V$_3$-C$_4$) W-L, $\Gamma$-X 3.25% 3.88</td>
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<td>(V$_3$-C$_5$) W-L 4.51% 3.93</td>
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<td>(V$_5$-C$_7$) W-L, $\Gamma$-X 5.15% 4.23</td>
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<td>(V$_5$-C$_8$) W-L 10.11% 3.98</td>
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<td>(V$_5$-C$_9$) W-L 4.07% 4.037</td>
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<td>(V$_7$-C$_1$) $\Gamma$-X-W 10.53% 3.81</td>
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(continued on next page)
Table 4 (continued)

<table>
<thead>
<tr>
<th>Optical structures</th>
<th>Peak position</th>
<th>Transition</th>
<th>Region</th>
<th>Percentage</th>
<th>Energy (eV)</th>
</tr>
</thead>
</table>
| E_5                | 6.04  
2.69% 8.44 | W-L, Γ-X  
4.78% 8.74 | X-W  
6.88% 6.56 | 6.95  
6.90 | 7.15  
6.90 |
|                    | 7.07  
3.59% 8.49 | W-L, Γ-X  
12.23% 6.83 | X-W-K  
16.15% 6.95 | 6.90  
6.90 | 7.00  
6.90 |
| E_6                | 6.49  
39.88% 5.91 | W-L, Γ-X  
9.72% 6.80 | X-W-K  
17.82% 6.06 | 6.90  
6.90 | 7.00  
6.90 |
|                    | 10.46  
20.60% 5.91 | W-L, Γ-X  
10.22% 6.66 | X-W-K  
13.82% 6.83 | 6.90  
6.90 | 7.00  
6.90 |
| E_7                | 6.82  
11.25% 6.68 | W-L, Γ-X  
8.51% 6.88 | X-W-K  
8.95% 6.47 | 6.90  
6.90 | 6.90  
6.90 |
|                    | 11.28  
11.17% 6.14 | W-L, Γ-X  
11.17% 6.14 | X-W-K  
11.17% 6.14 | 6.90  
6.90 | 6.90  
6.90 |
| E_8                | 7.66  
9.19% 6.14 | X-W-K  
9.19% 6.14 | 6.90  
6.90 | 6.90  
6.90 |
|                    | 5.26  
8.83% 6.80 | W-L, Γ-X  
8.83% 6.80 | X-W-K  
8.83% 6.80 | 6.90  
6.90 | 6.90  
6.90 |
| E_9                | 8.39  
11.25% 6.68 | W-L, Γ-X  
11.17% 6.14 | X-W-K  
11.17% 6.14 | 6.90  
6.90 | 6.90  
6.90 |
|                    | 2.93  
8.95% 6.47 | W-L, Γ-X  
8.95% 6.47 | X-W-K  
8.95% 6.47 | 6.90  
6.90 | 6.90  
6.90 |
| E_10               | 8.67  
3.59% 8.49 | W-L, Γ-X  
3.59% 8.49 | X-W-K  
7.36% 6.89 | 6.90  
6.90 | 6.90  
6.90 |
|                    | 3.34  
2.69% 8.49 | W-L, Γ-X  
2.69% 8.49 | X-W-K  
2.69% 8.49 | 6.90  
6.90 | 6.90  
6.90 |

The reflectivity spectra $R(u)$ of the studied compounds are represented in Fig. 6. The ZnRh$_2$O$_4$ (CdRh$_2$O$_4$) $R(u)$ reaches its maximal value of approximately 50% (40%) at approximately 7 eV in. The electron energy-loss function $L(u)$, which is an important factor describing the energy loss of fast electrons traversing a homogeneous dielectric material, is plotted in Fig. 6. The $L(u)$ primary peak location is usually associated with the plasma frequency $\omega_p$. A sharp maximum of the $L(u)$ spectrum located at approximately 11.4 eV (9.60 eV) is associated with the plasma oscillations in ZnRh$_2$O$_4$ (CdRh$_2$O$_4$). The $L(u)$ peak corresponds to the trailing edges in the reflection spectrum.

### 3.4. Elastic properties

Calculated elastic constants ($C_{ij}$) for ZnRh$_2$O$_4$ and CdRh$_2$O$_4$ are tabulated in Table 5 along with the theoretical results reported previously for CdRh$_2$O$_4$. There are no experimental data for the elastic constants for the two studied compounds. Theoretical prediction of the elastic constants are available only for the CdRh$_2$O$_4$ compound. The good agreement between our elastic constants values for the ZnRh$_2$O$_4$ and CdRh$_2$O$_4$ calculated using two different approaches proves the reliability of the obtained results. One can note that our calculated values for $C_{12}$ and $C_{13}$ are somewhat larger than those previously calculated for CdRh$_2$O$_4$ while the $C_{12}$ value is somewhat smaller than the reported one [15]. It is worth to note also that the previously reported results were obtained using the strain-stress method in the framework of pseudopotential plane wave approach, which is different from the used method in the present work. From Table 5, one can note:

(i) In both studied compounds, the $C_{11}$ value is higher than that of $C_{44}$, suggesting that the resistance of the studied compounds to unidirectional compression is higher than their resistance to shear deformation.

(ii) Calculated elastic constants $C_{ij}$ satisfy the Born and Huang mechanical stability criteria [40], suggesting that the examined systems are mechanically stable under elastic strain perturbations.
(iii) The sound wave velocities in a medium are related to some of its physical properties such as its thermal conductivity. The calculated sound wave velocities propagating along the [100], [110] and [111] cubic crystallographic directions of the investigated systems are gathered in Table 6. The propagation of the longitudinal sound waves is faster along the [100] direction than along the [110] and [111] ones, indicating that the [100] direction is the most rigid one.

(iv) The isotropic polycrystalline elastic constants, such as the bulk modulus \( B \), shear modulus \( G \), Young’s modulus \( E \) and Poisson’s coefficient \( \nu \), of the considered compounds are estimated from the obtained single-crystal elastic constants \( C_{ij} \) using the Voigt-Reuss-Hill approximation and the obtained results are listed in Table 5. From the computed values of the isotropic moduli, one can note the following:

(a) A good agreement between the bulk modulus value calculated from the \( C_{ij} \) and the corresponding one computed from the EOS fit for each studied system, proving the reliability of the obtained values of the single-crystal elastic constants (\( C_{ij} \)).

(b) According to Pugh’s empirical criterion [41], a material is malleable if the B/G ratio is greater than 1.75; otherwise, it is fragile. The calculated B/G ratio values; listed in Table 5, classify the title systems as ductile materials. Ductile materials are resistant to thermal shocks.

(c) Debye temperature \( \theta_D \) can be derived from the isotropic polycrystalline elastic moduli \( B \) and \( G \) using the known relationships [42]. As a rule, a high value of \( \theta_D \) implies a high thermal conductivity and high associated melting temperature. The calculated \( \theta_D \) values of for the studied compounds are listed in Table 5.

Table 5

<table>
<thead>
<tr>
<th>Property</th>
<th>( ZnRh_2O_4 )</th>
<th>( CdRh_2O_4 )</th>
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<tr>
<td>( C_{11} )</td>
<td>271</td>
<td>277</td>
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<tr>
<td>( C_{12} )</td>
<td>159</td>
<td>168</td>
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<tr>
<td>( C_{44} )</td>
<td>62</td>
<td>63</td>
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<tr>
<td>( B )</td>
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<td>59.6</td>
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<td>( G_r )</td>
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<tr>
<td>( E )</td>
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<td>( \sigma )</td>
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<td>164.6</td>
</tr>
<tr>
<td>( B/G )</td>
<td>3.30</td>
<td>3.44</td>
</tr>
<tr>
<td>( \theta_D )</td>
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<td>450</td>
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Table 6

<table>
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<th>System</th>
<th>( V_{100}^{100} )</th>
<th>( V_{100}^{110} )</th>
<th>( V_{100}^{111} )</th>
<th>( V_{110}^{100} )</th>
<th>( V_{110}^{101} )</th>
<th>( V_{110}^{111} )</th>
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<tbody>
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<td>( ZnRh_2O_4 )</td>
<td>Chapin 6372</td>
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<td>2896</td>
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<td>5871</td>
<td>2653</td>
<td>2109</td>
<td>5944</td>
<td>2305</td>
</tr>
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</table>
(iv) Evaluation of the elastic anisotropy extent in materials is of a great interest due to its implication in engineering science as well as in crystal physics. Indeed, the elastic anisotropy is highly correlated with the possibility to induce microcracks in materials [43] and has a significant influence on the nanoscale precursor textures in alloys [44]. Two different approaches were used to quantify the elastic anisotropy of the title compounds in the present work.

1. A universal index $A^U$, defined as follows [45]: $A^U = \frac{5(\frac{B_V}{G_V} + \frac{B_R}{G_R})}{C_0^6}$, where $B_V$ ($G_V$) and $B_R$ ($G_R$) represent the Voigt and Reuss estimations of $B$ ($G$), respectively, is widely used to measure the elastic anisotropy extent in crystals. For an isotropic single crystal, $A^U$ is equal to zero. Thus, the deviation of the magnitude of $A^U$ from zero measures the degree of the elastic anisotropy in the considered crystal. From Morreza method $C_{ij}$, we found that $A^U$ is equal to 0.025 for ZnRh$_2$O$_4$ and 0.257 for CdRh$_2$O$_4$, indicating that ZnRh$_2$O$_4$ is characterized by a weak elastic anisotropy while CdRh$_2$O$_4$ is characterized by a noticeable one.

2. A very practical way to estimate the elastic anisotropy in a material is by visualizing the dependence of its elastic moduli on the crystallographic directions. In an isotropic system, the 3D closed surface representing the dependence of the elastic modulus on the crystallographic directions should exhibit a spherical shape. Thus, the magnitude of the deviation of the 3D-representation of the crystallographic direction dependence of the elastic modulus from the spherical shape gives the extent of the elastic anisotropy. The crystallographic direction dependence of the Young’s modulus $E$ of a cubic crystal is given by the following relationship [46]:

$$E^{-1} = S_{11} - (2S_{11} - 2S_{12} - S_{44})(R_1^2 + R_2^2 + R_3^2)$$

$S_{ij}$ are the components of the elastic compliance matrix, $l_1$, $l_2$, and $l_3$ are the directional cosines with respect to the $x$-, $y$- and $z$-axes, respectively. Fig. 7 shows that the 3D-representation of the crystallographic direction dependence of the Young’s modulus of ZnRh$_2$O$_4$ deviates slightly from the spherical shape, indicating that this compound is characterized by a weak elastic anisotropy, while that of CdRh$_2$O$_4$ deviates noticeably from the spherical shape, revealing that this compound is characterized by a considerable elastic anisotropy. For more clear visualization of the elastic anisotropy, the cross-sections of the 3D closed surfaces in the [001] plane of the examined compounds are also shown in Fig. 7. One can note that the deviation of the cross section from the circle is slight for ZnRh$_2$O$_4$, indicating its low elastic anisotropy, whereas this deviation is considerable for CdRh$_2$O$_4$, indicating the high elastic anisotropy of CdRh$_2$O$_4$.

3.5. Thermoelectric properties

Thermoelectric materials (TE) efficiently convert heat to
electricity and thereby are of great interest for energy applications. The thermoelectric performance of TE is characterized by a dimensionless parameter called figure of merit $ZT$ defined as $ZT = S^2\sigma/(k_e + k_l)$, where $S$, $\sigma$, $T$, $k_e$ and $k_l$ are the Seebeck coefficient (called also thermopower), electrical conductivity, absolute temperature, electronic thermal conductivity and lattice thermal conductivity, respectively. A high $ZT$ requires a combination of high electrical conductivity with low thermal conductivity and high Seebeck coefficient. Though there is no theoretical upper limit of $ZT$, it is challenging to achieve higher values because the three conflicting transport parameters $S$, $\sigma$ and $\kappa$ [47]. Therefore, an efficient TE can be designed by optimizing its thermoelectric parameters $S$, $\sigma$ and $\kappa$. Fig. 8 illustrates the charge-carrier concentration dependence of the Seebeck coefficient ($S$), electrical conductivity scaled by relaxation time ($\sigma/\tau$), electronic thermal conductivity scaled by relaxation time ($k_e/\tau$), power factor ($PF = S^2\sigma/\tau$) and the thermoelectric figure of merit $ZT_e = S^2\sigma T/k_e$ for both the $n$-type and $p$-type doped ZnRh$_2$O$_4$ and CdRh$_2$O$_4$ compounds at three fixed temperatures, namely $T$: 300, 600 and 900 K. We have investigated the transport properties of the considered compounds for a charge-carrier concentration between $10^{17}$ cm$^{-3}$ and $10^{21}$ cm$^{-3}$, which is an optimum charge-carrier concentration range for better thermoelectric performance. Fig. 8 shows that the magnitude of Seebeck coefficient $S$ decreases with increasing carrier concentration and increases with increasing temperature for both the $n$-type and $p$-type doped compounds. This is a common trend in the thermoelectric materials. One can note that at the same temperature and charge-carrier concentration, the magnitude of $S$ for the $p$-doped system is larger than that of the $n$-doped one throughout the studied charge-carrier concentration range. This might be because

Fig. 8. Variation of the Seebeck coefficient ($S$), electrical conductivity over relaxation time ($\sigma/\tau$), electronic thermal conductivity over relaxation time ($k_e/\tau$), power factor ($PF$) and figure of merit ($ZT_e$) as functions of charge-carrier concentration for the $n$-type and $p$-type doping ZnRh$_2$O$_4$ and CdRh$_2$O$_4$ for different fixed temperatures.
the valence bands at the VBM are less dispersive than the conduction bands at the CBM, i.e., the hole effective mass at the VBM is larger than the electron one at the CBM. Thus, one can expect that the \( p \)-type doped ZnRh\(_2\)O\(_4\) and CdRh\(_2\)O\(_4\) are more favourable for thermoelectric performance than the \( n \)-type doped ones. The thermopower \( S \) shows practically the same behavior regarding the variation of carrier concentration and temperature for the two studied oxide spinels. This behavior might be attributed to the similarity of their energy band dispersions around the Fermi level. For both studied compounds, the electrical and electronic thermal conductivities scaled by relaxation time \( (\sigma/\tau \text{ and } k_e/\tau) \) increase with increasing carrier concentration for both holes and electrons. At the same temperature and charge-carrier concentration, the electrical and thermal conductivities of the electrons are larger than those of the holes for both investigated compounds. This result is expected because the hole effective masses at the VBM are larger than those of the electrons at the CBM. At the same temperature and charge-carrier concentration, the maximum figure of merit \( (ZT) \) of the hole-doped systems are slightly larger than that of the electron-doped ones. The figure of merit \( ZT \) reaches a maximum of approximately 1 for a hole concentration of \( 1 \times 10^{17} \text{cm}^{-3} \). To shed light on the quality of the thermopower \( S \) of ZnRh\(_2\)O\(_4\) and CdRh\(_2\)O\(_4\), we compared the values of their Seebeck coefficients with that of the bismuth telluride alloy Bi\(_2\)Te\(_3\), a traditional thermoelectric material. At \( T = 300 \text{K} \) and charge-carrier concentration of \( 4 \times 10^{18} \text{cm}^{-3} \), the Seebeck coefficient \( S \) is equal to 313 \( \mu \text{VK}^{-1} \) for the \( p \)-type Bi\(_2\)Te\(_3\) and to \(-196 \mu \text{VK}^{-1}\) for the \( n \)-type one \cite{48}. Under the same conditions, \( S \) is equal to 667 (745) \( \mu \text{VK}^{-1} \).

**Fig. 9.** Variation of the Seebeck coefficient \( (S) \), electrical conductivity over relaxation time \( (\sigma/\tau) \), electronic thermal conductivity over relaxation time \( (k_e/\tau) \), power factor \( (PF) \) and figure of merit \( (ZT) \) as functions of temperature for the \( n \)-type and \( p \)-type doping ZnRh\(_2\)O\(_4\) and CdRh\(_2\)O\(_4\) for different fixed charge-carrier concentrations.
for the $p$-type ZnRh$_2$O$_4$ (CdRh$_2$O$_4$) and $-501 (-502)$ $\mu$VK$^{-1}$ for the $n$-type one. Therefore, one can appreciate that the Seebeck coefficients of ZnRh$_2$O$_4$ and CdRh$_2$O$_4$ are greater than that of the traditional thermoelectric compound Bi$_2$Te$_3$. So, one can claim that the spinel oxides ZnRh$_2$O$_4$ and CdRh$_2$O$_4$ are potential candidates for thermoelectric applications if one can further reduce their thermal conductivities via some techniques, such as alloying, nanostructuring, or superlattice growth.

To explore the temperature effect on the thermoelectric properties of the title compounds, temperature dependence of the Seebeck coefficient, electrical and thermal conductivities scaled by relaxation time and figure of merit were calculated for both $n$-type and $p$-type compounds at fixed charge-carrier concentrations ($1 \times 10^{18}$ cm$^{-3}$, $1 \times 10^{19}$ cm$^{-3}$, $1 \times 10^{20}$ cm$^{-3}$ and $1 \times 10^{21}$ cm$^{-3}$). From Fig. 9, one can note that for a charge-carrier concentration fixed at $1 \times 10^{18}$ cm$^{-3}$, the thermoelectric performance of the considered compounds practically does not vary with temperature over a wide temperature range.

### 3.6. Thermodynamical properties

Thermodynamic properties of the spinel oxides XRh$_2$O$_4$ ($X = Zn$, Cd), including pressure and temperature dependences of the lattice parameter, bulk modulus, volume expansion coefficient and Debye temperature, were investigated via the quasi-harmonic Debye model as implemented in the Gibbs program [49]. Theoretical details of the quasi-harmonic Debye model are available in Ref. [49].

Temperature dependence of the lattice parameter ($a$) and bulk modulus ($B$) for the XRh$_2$O$_4$ ($X = Zn$, Cd) spinels at some fixed pressures (0, 5, 10, 15 and 20 GPa) are depicted in Fig. 10. $a$ and $B$ are nearly constant for temperature lower than 100 K. For temperature higher than 100 K, $B$ decreases and $a$ increases with increasing temperature at a fixed pressure, while $B$ increases and $a$ decreases with increasing pressure at a fixed temperature. One can note that the increase propensity of the lattice parameter with temperature slightly decreases with increasing pressure. The effect of increasing pressure on the lattice parameter and bulk modulus is the same as that of decreasing temperature. At zero pressure and ambient temperature, $B$ ($a$) is approximately equal to 181 GPa (10.1767 Å) in ZnRh$_2$O$_4$ and 173 GPa (10.4881 Å) in CdRh$_2$O$_4$.

Fig. 11 shows the temperature dependence of the volume thermal expansion coefficient ($\alpha$) at some fixed pressures (0, 5, 10, 15 and 20 GPa) for ZnRh$_2$O$_4$ and CdRh$_2$O$_4$. For temperature $T < 200$ K, $\alpha$ increases sharply with increasing temperature at a fixed pressure, especially at zero pressure. For temperature $T > 200$ K, the propensity of increase of $\alpha$ becomes weaker and it gradually tends to a linear increase except for zero pressure. The volume thermal expansion coefficient decreases strongly with increasing pressure. From Fig. 11, one can observe that for $P = 20$ GPa and $T > 200$ K, the expansion coefficient increases very slowly with increasing temperature, which means that under high pressure the effect of temperature on $\alpha$ is suppressed. At zero pressure and room temperature, $\alpha$ is approximately equal to $4.64 \times 10^{-5}$ K$^{-1}$ in ZnRh$_2$O$_4$ and $4.32 \times 10^{-5}$ K$^{-1}$ in CdRh$_2$O$_4$.

Fig. 12 shows the temperature dependence of the isochoric ($C_V$) and isobaric ($C_P$) heat capacities at some fixed pressures (0, 5, 10, 15 and 20 GPa). At low temperature ($T < 150$ K), $C_P$ and $C_V$ are proportional to $T^3$ in agreement with the standard elastic continuum theory [50]. The difference between $C_V$ and $C_P$ is very slight. Both $C_V$ and $C_P$ increase with increasing temperature at a given pressure and decrease as pressure rises at a given temperature. For temperature lower than 400 K, $C_V$ and $C_P$ increase sharply with increasing temperature. For temperature higher than 400 K, the increase of $C_V$ gradually slows and it tends to the Dulong-Petit limit (349.21 Jmol$^{-1}$K$^{-1}$), indicating that all the phonon modes are excited. The variation feature of the $C_V$ is similar to that of $C_P$ in the low temperature region, both of them are increasing with temperature; this is due to the anharmonic approximations. However, in the high temperature range, the anharmonic effect on $C_V$ is
suppressed, the change tendency of $C_P$ exhibits apparently different features; it increases with increasing temperature and do not converge to a constant value. From Fig. 12, one can note that temperature and pressure have opposite influences on the heat capacity and the effect of temperature on the heat capacity is more significant than that of pressure. The value of $C_V (C_P)$ at 300 K and zero pressure is 319.21 J mol$^{-1}$K$^{-1}$ (330.19 J mol$^{-1}$K$^{-1}$) for ZnRh$_2$O$_4$ and 327.94 J mol$^{-1}$K$^{-1}$ (337.90 J mol$^{-1}$K$^{-1}$) for CdRh$_2$O$_4$.

Debye temperature is a fundamental thermodynamical parameter that is directly related to many physical properties of solids, such as elastic constants, melting temperature and specific heat. Temperature dependence of Debye temperature $\theta_D$ at some fixed pressures (0, 5, 10, 15 and 20 GPa) is displayed in Fig. 13. Debye temperature $\theta_D$ is nearly constant in the 0–100 K range and then decreases with increasing temperature. The propensity of the increase of $\theta_D$ decreases with increasing pressure. Calculated $\theta_D$ at zero pressure and temperature is equal to 414.5 K for ZnRh$_2$O$_4$ and 345.3 K for CdRh$_2$O$_4$. It is worth to note that the ZnRh$_2$O$_4$ and CdRh$_2$O$_4$ Debye temperature values calculated using the quasi-harmonic Debye model are in good agreement with the corresponding ones derived from the elastic constants (450 K for ZnRh$_2$O$_4$ and 348 K for CdRh$_2$O$_4$). This might be an indication that the quasi-harmonic Debye model is a very reasonable alternative to account for the thermal effects with no expensive task in terms of computational time.

4. Conclusions

In summary, the structural, electronic, optical, elastic, thermoelectric and thermodynamic properties of the XRh$_2$O$_4$ (X = Zn, Cd) oxide spinels were studied using the full potential linearized augmented plane wave plus local orbitals (FP-LAPW+lo) approach within the framework of density functional theory. The optimized structural parameters of the title compounds obtained using the GGA-PBEsol to model the exchange-correlation energy are in
excellent agreement with the available experimental data. The calculated band structures reveal that both studied compounds are indirect band gap semiconductors. The calculated ZnRh$_2$O$_4$ band gap using the TB-mBJ is in good agreement with the available experimental data. Analysis of the DOS diagrams reveals that the origin of the band gap in the ZnRh$_2$O$_4$ (X = Zn, Cd) spinels is due to the ligand field splitting of the Rh-4d into fully occupied $\Gamma_{2g}$ and empty levels $\Gamma_{4d}$. The calculated charge-carrier effective masses show that the valence band holes are heavier than the conduction band electrons. Linear optical functions, including dielectric function, refractive index, extinction coefficient, reflectivity, absorption coefficient, energy-loss function were calculated, and the critical points in the optical spectra are assigned to the electronic interband transitions according to the calculated band structure. It is found that the occupied $\Gamma_{4d}$ and empty $\Gamma_{2g}$ states and the energy levels $\Gamma_{4d}$ play the major role in the optical transitions as initial and final states, respectively. The electronic and optical spectra of the two considered compounds have rather similar shapes. There are no available experimental data for the elastic properties of the title materials, so our results are pure theoretical predictions. The agreement between the calculated elastic constants using two different methods could prove the reliability of the reported results. The predicted elastic moduli suggest that the examined spinels are mechanically stable and ductile materials. ZnRh$_2$O$_4$ exhibits a weak elastic anisotropy while CdRh$_2$O$_4$ demonstrates a noticeable elastic anisotropy. The elastic wave velocities and Debye temperature are numerically estimated from the calculated elastic constants. Charge-carrier concentration dependence of the thermoelectric parameters, including the Seebeck coefficient, electronic conductivity, thermal conductivity and figure of merit, was explored. The calculated Seebeck coefficient values demonstrate that the p-type title compounds are more favourite for thermoelectric performance than the n-type ones. The obtained results suggest that the spinel oxides ZnRh$_2$O$_4$ and CdRh$_2$O$_4$ are potential candidates for thermoelectric applications if one can further reduce their thermal conductivities via some techniques.

Acknowledgment

The authors (A. Bouhemadou and S. Bin–Omran) extend their appreciation to the International Scientific Partnership Program ISPP at King Saud University for funding this research work through ISPP# 0025.

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