Journal of Nano- and Electronic Physics
Vol. **13** No 5, 05025(5pp) (2021)

Журнал нано- та електронної фізики
Том **13** № 5, 05025(5cc) (2021)

Ab Initio Study of Electronic, Magnetic and Optical Properties of $CuRh_2O_4$ Spinel: First Principles Calculation

Radia Bencheikh[1,*], Karima Belakroum[1], Yamina Benkrima[2]

[1] *Laboratory of the Development of New and Renewable Energies in Arid Zones, Ouargla university, 30000 Ouargla, Algeria. Kasdi Merbah-Ouargla university, Mathematics and Materials Science faculty, Physics department, route de Ghardaia, Ouargla 30000, Algeria*
[2] *Ecole normale supérieure of Ouargla, Algeria*

(Received 25 July 2021; revised manuscript received 20 October 2021; published online 25 October 2021)

In this work, the structural, electronic, magnetic, and optical properties of spinel $CuRh_2O_4$, which has tetragonal ordering (I41/amd), were studied at room temperature using density functional theory (DFT) and SIESTA code with ultra-soft pseudopotential method. Indeed, it is a useful method to predict the crystal structures of spinel $CuRh_2O_4$. The crystal structures were optimized using a generalized gradient approximation (GGA) according to the scheme described by Perdew-Burke-Ernzerhof (PBE) and analyzed on the basis of density of states (DOS), projected density of states (PDOS), and band structure. The calculated structural parameters of this compound are consistent with the available experimental data, so these results can be considered as predictions. The overlapping of the valence and conduction bands at the Fermi level indicates that $CuRh_2O_4$ has a metallic nature. There is strong hybridization between the Cu 3*d* and O 2*p* orbitals, as well as between the Rh 4*d* and O 2*p* orbitals. The magnetic contribution of $CuRh_2O_4$ atoms is higher for Rh atoms in the 4*d* orbital, it also exists for Cu atoms in the 3*d* orbital. Concerning O atoms, there is a small contribution at the 2*p* orbital level. The total magnetic moment of atoms is estimated at 1.98 μ_B. These results indicate that $CuRh_2O_4$ can absorb all frequencies between visible light and extreme UV region. Comparison of the calculated lattice parameters and other properties with the available experimental values revealed compatibility between them. These results are in broad agreement with the experimental results.

Keywords: Spinel, Density functional theory (DFT), Electronic properties, Magnetic properties, Optical properties.

DOI: 10.21272/jnep.13(5).05025 PACS numbers: 71.20. – b, 78.20.Ci

1. INTRODUCTION

The spinel compounds of AB_2O_4 family (such as $CoRh_2O_4$, $CuRh_2O_4$, $NaRh_2O_4$, etc.) are significant in the field of materials science and engineering due to their widely relevant and outstanding properties [1].

Spinels have the general formula AB_2O_4, where A can be Cu, Na, etc. and B – Rh, etc. A first-order phase transition from a tetragonal to a cubic structure took place. A high-temperature cubic structure is an ordinary spinel shown in Fig. 1 [2] ($Fd\bar{\bar{3}}m$, $a = 8.5487$ Å), while at room temperature the structure can be described as a distorted spinel (I41/amd, $a = 6.1707(4)$ Å, $c = 7.9183(7)$ Å) [2, 3], Cu and Rh occupy exclusively tetrahedral and octahedral sites, respectively. Room-temperature Jahn-Teller distortion has been described by both X-ray and neutron diffraction as a tetragonally distorted spinel [4-6] with space group I41/amd, shown in Fig. 2. Using room temperature in this study [4], neutron diffraction in a normal spinel yields A and B cations. In inverse spinels, the A atoms occupy half of the octahedral sites, while the B ones are equally shared by the octahedral and tetrahedral sites.

Spinel $CuRh_2O_4$ (I41/amd) is studied by density functional theory (DFT) [7] through generalized gradient approximation (GGA). GGA together with the Perdew-Burke-Ernzerhof (PBE) functional [8] describe these materials to be metallic. The fact that the valence and conduction bands overlap each other at the Fermi level reveals the metallic nature of $CuRh_2O_4$.

The different optical functions are also clearly observed. Absorption spectra indicate that $CuRh_2O_4$ is suitable for solar cell use, and the reflectivity spectrum shows how these compounds can be prominent reflector materials. The aim of the present study is to theoretically predict the structural, electronic, optical, and magnetic properties of $CuRh_2O_4$ spinel, providing referential data for further experimentations, uncovering its potential for technological applications, as well as completing existing information in this field. This research paper focuses on the electronic and magnetic properties, reports the results on the electronic structure, and discusses the optical properties calculations within the framework of the GGA-PBE [8] and DFT [7]. It is outlined as follows. First, Section 3.1 describes the method and relevant computational parameters used in the calculations. Then, in Section 3.2, the calculated results of the electronic properties of these oxides are discussed in terms of band structure and density of states (DOS), with the addition of an analysis of the optical properties in Section 3.3. Finally, Section 4 provides a summary of the study.

2. CALCULATION METHODS

This study is based on the ab initio method using DFT [7]. All calculations were executed using the SIESTA simulation package [9]. Both the GGA-PBE [8]

---

[*] radiabencheikh01@gmail.com

and the PBE scheme were treated by the pseudopotential method [10]. For comparison purposes, the all-electron variant was used to treat the tetragonal phase. A set of 122 (9×3×3) *k*-points was also used to perform a reliable integration over the Brillouin zone (BZ). A cutoff parameter RMT $K_{\max} = 150$ Ry, where RMT is the smallest sphere and $K_{\max}$ is the largest reciprocal lattice vector, was used in the plane wave expansion. These values were obtained owing to the total energy convergence. The valence electron configurations of $CuRh_2O_4$ were the following: $(Cu:4s^3d^9)O:2s^22p^4)(Rh:5s^24d^7)$.

3. RESULTS AND DISCUSSION

3.1 Structural Analysis

$CuRh_2O_4$ crystallizes in a closely packed tetragonal crystal structure, space group I41/amd (n. 141). The unit cell of $CuRh_2O_4$ contains 4 Cu atoms positioned at (0; 1/4; 7/8), 8 Rh atoms at (0; 0.5; 0.5) and 16 O atoms at (0; 0.4693; 0.2413), see Fig. 2. The crystal structures ($a = b = 6.1756$ Å and $c = 7.9006$ Å) [11] were optimized. In order to visualize this system, XCrySDen graphic software, which is a program for visualizing crystalline and molecular structures, was used [12].

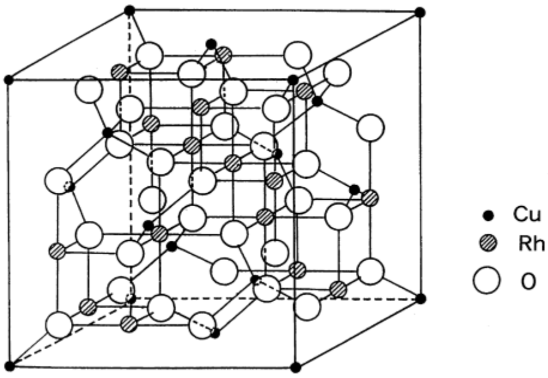

Fig. 1 – The cubic unit cell of the spinel structure [13]

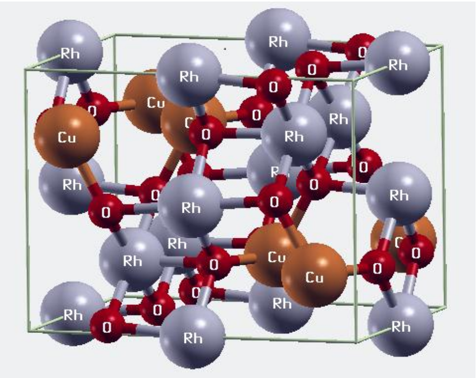

Fig. 2 – Tetragonal crystal structure of spinel $CuRh_2O_4$

The lattice constants calculated by GGA [8] are given in Table 1.

The results presented in Table 1 are in good agreement with the experimental results of the references listed in Table 1. Since we did not find a theoretical study for this compound to compare with our results, we can consider our results as a reference for other theoretical studies.

This is the first study of compound $CuRh_2O_4$ using DFT, since this compound has not been studied before, therefore it is the reference for other studies.

Table 1 – Calculated lattice constants (a, b and c in Å, V in Å^3 and E_{coh} in eV) of $CuRh_2O_4$

Space Group	I41/amd
Compound	$CuRh_2O_4$
Lattice constants Present work (GGA)	$a = 6.21$ Å, $b = 6.21$ Å, $c = 7.957$ Å ($V = 303.179$ Å^3), $E_{coh} = -6.31$ eV
Expt. [5, 6, 11]	$a = 6.1709$ Å, $b = 6.1709$ Å, $c = 7.9183$ Å ($V = 301.179$ Å^3), $E_{coh} = -6.57$ eV

3.2 Electronic and Magnetic Properties

The electronic properties of $CuRh_2O_4$ were calculated via energy bands and the total density of states (TDOS). In this study, the band structure along highly symmetric directions in the BZs, as well as the TDOS and partial DOS (PDOS) of $CuRh_2O_4$, were calculated. The electronic band structure of spinel $CuRh_2O_4$ (I41/amd) calculated using GGA-PBE is shown in Fig. 5. These non-zero values of the band structure manifest the metallic nature of $CuRh_2O_4$ with evidence of zero band gap.

Fig. 3 and Fig. 4 show, respectively, the calculated TDOS and PDOS of $CuRh_2O_4$ using GGA-PBE. The TDOS determines the number of electron orbitals per unit energy. The Fermi level position is taken as a reference point to determine TDOS (Fig. 3).

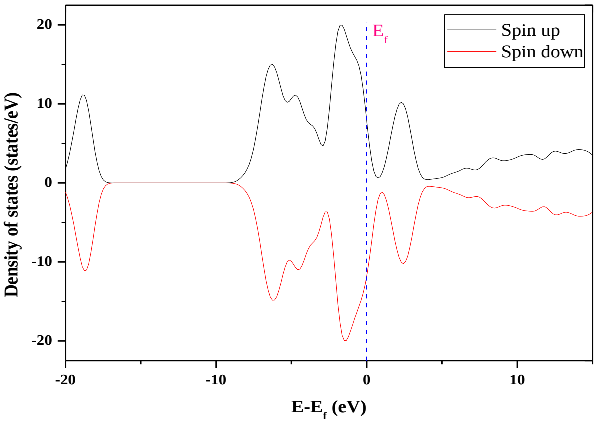

Fig. 3 – TDOS of $CuRh_2O_4$ calculated by DFT within GGA, the Fermi level E_f is indicated by the vertical line

It is seen from Fig. 3 that the TDOS is divided into four spin regions. The first is a sharp peak located at around – 1.95 eV. In Fig. 4, the PDOS spectra of spin channels arise mainly from the filled Cu 3*d* and Rh 4*d* orbitals, adding O 2*p* orbitals to the light contribution. The second region is the peak at – 6 eV, the third is at – 16 eV, and the fourth is at 3.1 eV.

The lowest energy band lying in the range from – 9.7 to – 3.90 eV arises mainly due to hybridization of O 2*p* orbitals, and in the range from – 21 to – 17.4 eV – of O 2*s* orbitals. A higher DOS value at – 2.99 eV manifests hybridization of Cu 3*d* orbitals, as well as hybridization of Rh 3*d* at – 3.8 eV and – 0.63 eV, see Fig. 4.

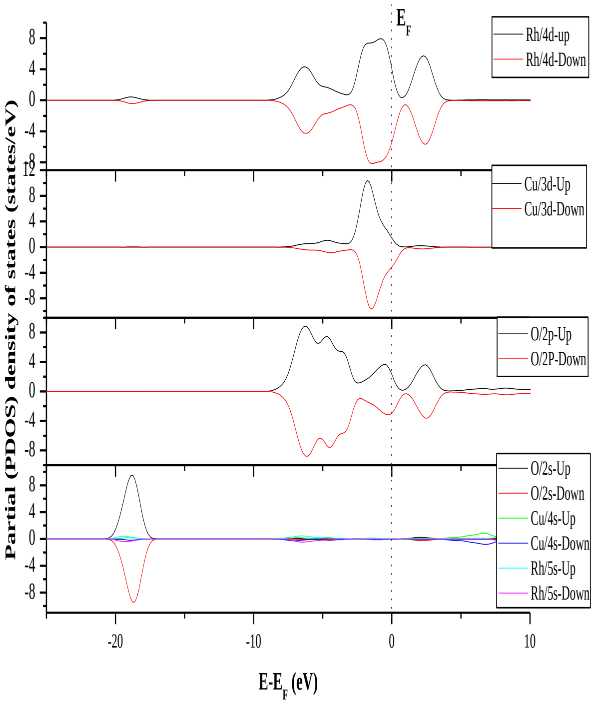

Fig. 4 – PDOS of the tetragonal structure of $CuCr_2O_4$ within GGA-PBE

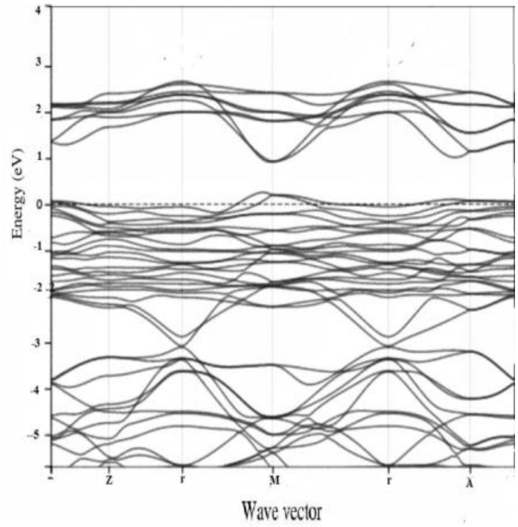

Fig. 5 – Band structure of $CuRh_2O_4$ within GGA-PBE

The PDOS determines the occupied electron orbitals per unit energy coming from individual atoms. The Cu 3*d* electrons provide PDOS of 8.05 orbitals/eV per unit cell at the Fermi level, as presented in Fig. 4. In addition, it is seen in Fig. 4 that the values of PDOS reach 7.94 orbitals/eV per unit cell for Rh 4*d* electrons and 8.03 orbitals/eV for O 2*p* electrons.

Fig. 4, bearing PDOS, demonstrates the magnetic contribution of $CuRh_2O_4$ atoms. Actually, this contribution is higher for Rh atoms, appearing in the 4*d* orbital. It also exists for Cu atoms in the 3*d* orbital. Concerning O atoms, there is a small contribution at the 2*p* orbital level. The total magnetic moment of atoms is estimated at 1.98 μB.

The horizontal dotted line between the valence and conduction bands considers the Fermi level. Fig. 5 on the band structure shows that the valence and conduction bands overlap each other at the Fermi level. Actually, only a few bands (colored lines) crossed the Fermi level, because no band gap appears between the valence and conduction bands (see Fig. 3 and Fig. 4). This indicates that $CuRh_2O_4$ has metallic conductivity.

3.3 Optical Properties

It is known that the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ [14] is mainly connected with the electronic response. The imaginary part $\varepsilon_2(\omega)$ of the dielectric function is calculated from the momentum matrix elements between the occupied and unoccupied waves, as given in [15]:

$$\varepsilon_2(\omega) = \frac{Ve^2}{2\hbar\pi m^2 m\omega^2} \int d^3k \sum \int \left|\psi_c\right| p \left|\psi_\upsilon\right|^2 \delta\left(Ec - E\upsilon - \hbar\omega^2\right) , \quad (1)$$

where *k* is the absorption index, *δ* is the absorption coefficient, *E* is the energy of the electron, *V* is the unit cell volume, *P* is the momentum operator, ħ is the reduced Planck constant, ψ_c and ψ_υ are the wave functions of the conduction and valence bands.

Then, the real part $\varepsilon_1(\omega)$ can be obtained from the Kramers-Kronig relationship [16]:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} M \int_0^\infty \frac{\varepsilon_2(\omega')\omega'}{\omega'^2 - \omega^2} d\omega , \quad (2)$$

where *M* is the principal value of the integral.

All other optical properties, such as the reflectance, optical conductivity $\sigma(\omega)$, refractive index (*n*), and absorption index (*k*) are derived from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ [17].

The absorption coefficient is an important parameter that measures the absorption of the electromagnetic wave energy, while traversing the unit thickness of a material [18]; it depends on the wavelength of the electromagnetic wave and the material as well. Fig. 6 shows the plotted absorption coefficient spectrum of $CuRh_2O_4$.

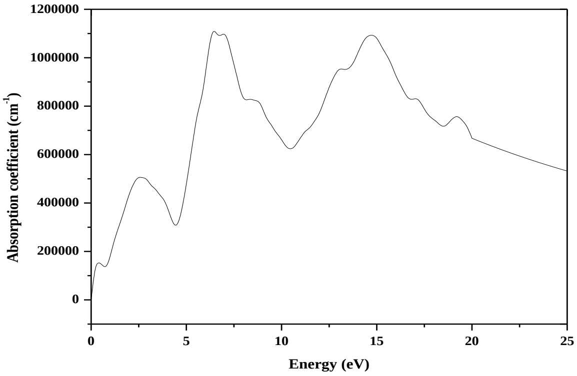

Fig. 6 – Absorption coefficient spectrum of $CuRh_2O_4$

A wide range of absorption, from visible light to UV with a maximum at 7.1 eV, is observed. Furthermore, at high energies, $CuRh_2O_4$ exhibits absorption in the energy range from 5 to 10 eV and from 11 to 25 eV.

Accordingly, these results indicate that $CuRh_2O_4$ can absorb all frequencies between visible light and extreme UV region. Fig. 7 shows the calculated imaginary part $\varepsilon_2(\omega)$ of the dielectric function for an incident photon energy ($h\omega$) in the 0-3 eV range.

The $\varepsilon_2(\omega)$ curve drops off rapidly with increasing photon energy. With a further increase in the photon energy from 2-10 eV, the refractive index $n(\omega)$ spectra are shown in Fig. 8.

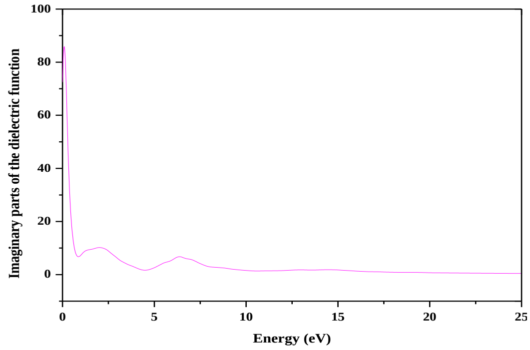

Fig. 7 – Imaginary part $\varepsilon_2(\omega)$ of the dielectric function

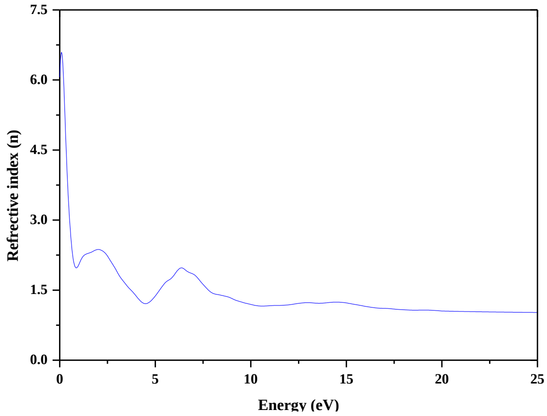

Fig. 8 – Refractive index $n(\omega)$ spectra

The real part of the refractive index, known as the phase velocity, which has shifted in Fig. 8 in the whole graph at zero energy point refractive index value, is high for $CuRh_2O_4$. The static value of the refractive index is 6.8 for $CuRh_2O_4$ in the IR region.

The static refractive index $n(0)$ is equal to ~ 6.8.

The $n(\omega)$ spectrum increases from the static value to small peaks in the visible light region and reaches a maximum of 2.3 in the UV region, and then decreases rapidly with increasing photon energy to its minimum value, which is smaller than the one in the UV region.

The reflectivity function calculated as shown in Fig. 9 demonstrates good reflectivity in the IR and UV regions. The overall reflectivity found for the material is suitable to use as a reflector material.

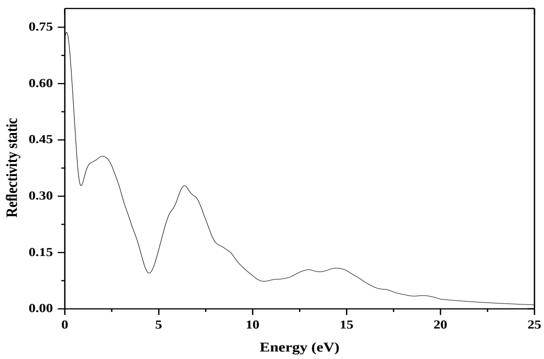

Fig. 9 – Reflectivity function $R(x)$

4. CONCLUSIONS

This study aimed at establishing a clearer picture of the electronic structure, magnetic and optical properties of $CuRh_2O_4$ spinel compound. The calculations were performed using ab initio GGA for exchange correlation implemented in the SIESTA code at 0 K. A detailed comprehensive study was carried out, and the results are summed up as follows:

1. The calculated structural parameters of this compound are consistent with the available experimental data; so, these results can be considered as predictions.
2. The valence and conduction bands overlap each other at the Fermi level. This indicates that $CuRh_2O_4$ has a metallic nature.
3. There is strong hybridization between the Cu 3*d* and O 2*p* orbitals, as well as between the Rh 4*d* and O 2*p* orbitals.
4. The calculated total magnetic moments are found to be 1.98 μB.
5. These results indicate that $CuRh_2O_4$ can absorb all frequencies between visible light and extreme UV region.

REFERENCES

1. S.K. Sharma, D. Gourier, B. Viana, T. Maldiney, E. Teston, D. Scherman Richard, *Opt. Mater.* **36**, 1901 (2014).
2. W.A. Dollase, H.St.C. O'Neill, *Acta. Crystallographica* **C53**, 657 (1997).
3. L. Ge, J. Flynn, J.A.M. Paddison, M.B. Stone, S. Calder, M.A. Subramanian, A.P. Ramirez, M. Mourigal, *Phys. Rev. B* **96**, 064413 (2017).
4. R.A. Endoh, O.b. Fujishima, T.B. Atake, N.A. Matsumoto, M.A. Hayashi, S.A. Nagata, *J. Phys. Chem. Solids* **60**, 457 (1999).
5. Di Gui, L. Ji, A. Muhammad, W. Li, W. Cai, Y. Li, X. Li, X. Wu, P. Lu, *J. Phys. Chem. Lett.* **9**, 751 (2018).
6. A.V Zakrzewski, S. Gangopadhyay, G.J. MacDougall, A.A. Aczel, S. Calder, T.J. Williams, *Phys. Rev. B* **97**, 214411 (2018).
7. P. Ordejón, E. Artacho, J.M. Soler, *Phys. Rev. B* **53**, 10441 (1996).
8. J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77** No 18, 3865 (1996).
9. J.M. Soler, E. Artacho, J.D. Gale, A. García, J. Junquera, P. Ordejón, D. Sánchez-Portal, *J. Phys. Condens. Matter.* **14** No 11, 2745 (2002).
10. N. Troullier, J.L. Martins, *Phys. Rev. B.* **43** No 3, 1993 (1991).
11. B. Ismunandar, B.J. Kennedy, Brett. A. Hunter, *Mater. Res. Bull.* **34**, 135 (1999).
12. A. Kokalj, *Computer. Mater. Sci.* **28**, 155 (2003).
13. R. Endoh, O. Fujishima, T. Atake, N. Matsumoto, M. Hayashi, S. Nagata, *J. Phy. Chem. Solids* **60**, 458 (1999).
14. C. ZhiBin, T. Honglin, Y. Lan, C. Xiang, *Eur. Phys. J. B* **88**, 281 (2015).
15. T. BenNasr, H. BenAbdallah, R. Bennaceur, *Physica B* **405**,

3427 (2010).
16. S. Akbudak, A.K. Kushwaha, G. Uğur, Ş. Uğur, H. Yaşar Ocak, *Ceramics Int.* **44**, 310 (2018).
17. J. Sun, H.T. Wang, J.L. He, Y.J. Tian, *Phys. Rev. B* **71**, 125132 (2005).
18. J. Sun, X.-F. Zhou, Y.-X. Fan, J. Chen, H.-T. Wang, X. Guo, H Julong, Y. Tian, *Phys. Rev. B* **73**, 045108 (2006).

Ab initio дослідження електронних, магнітних та оптичних властивостей шпінелі $CuRh_2O_4$: розрахунок з перших принципів

Radia Bencheikh[1], Karima Belakroum[1], Yamina Benkrima[2]

[1] *Laboratory of the Development of New and Renewable Energies in Arid Zones, Ouargla university, 30000 Ouargla, Algeria. Kasdi Merbah-Ouargla university, Mathematics and Materials Science faculty, Physics department, route de Ghardaia, Ouargla 30000, Algeria*
[2] *Ecole normale supérieure of Ouargla, Algeria*

У роботі структурні, електронні, магнітні та оптичні властивості шпінелі $CuRh_2O_4$, яка має тетрагональне впорядкування (I41/amd), були вивчені при кімнатній температурі за допомогою теорії функціонала густини (DFT) та коду SIESTA за методом надм'якого псевдопотенціалу. Дійсно, цей метод є корисним для прогнозування кристалічних структур шпінелі $CuRh_2O_4$. Кристалічні структури були оптимізовані за допомогою узагальненого градієнтного наближення (GGA) за схемою, описаною Пердью-Берком-Ернзергофом (PBE), та проаналізовані на основі густини станів (DOS), прогнозованої густини станів (PDOS) та зонної структури. Розраховані структурні параметри цієї сполуки узгоджуються з наявними експериментальними даними, тому отримані результати можна розглядати як прогнози. Перекриття валентної зони та зони провідності на рівні Фермі вказує на те, що $CuRh_2O_4$ має металеву природу. Існує сильна гібридизація між орбіталями Cu 3*d* та O 2*p* і орбіталями Rh 4*d* та O 2*p*. Магнітний внесок атомів $CuRh_2O_4$ вищий для атомів Rh на 4*d*-орбіталі, він також існує для атомів Cu на 3*d*-орбіталі. Стосовно атомів O, є невеликий внесок на орбітальному рівні 2*p*. Загальний магнітний момент атомів оцінюється в 1,98 μ_B. Ці результати показують, що $CuRh_2O_4$ може поглинати всі частоти між видимим світлом та крайньою УФ-областю. Порівняння розрахованих параметрів ґратки та інших властивостей з наявними експериментальними значеннями виявило їх сумісність. Ці результати цілком узгоджуються з результатами експерименту.

Ключові слова: Шпінель, Теорія функціонала густини (DFT), Електронні властивості, Магнітні властивості, Оптичні властивості.