

Article

Spin-Polarized Study of the Structural, Optoelectronic, and Thermoelectric Properties of the Melilite-Type $\text{Gd}_2\text{Be}_2\text{GeO}_7$ Compound

Fafa Chiker ¹, Najet Baki ¹, Yasser Abderrahim Khachai ², Houari Khachai ^{1,*}, Redouane Miloua ³, Rabah Khenata ^{4,*}, Saad Bin-Omran ⁵, Abdelmadjid Bouhemadou ⁶, Mohammed Benali Kanoun ⁷ , and Souraya Goumri-Said ^{8,*} 

- ¹ Laboratoire d'Etude des Matériaux et Instrumentations Optiques (LEMIO), Université Djillali Liabès de Sidi Bel-Abbès, Sidi Bel-Abbès 22000, Algeria
- ² Condensed Matter and Sustainable Development Laboratory (LMCDD), Université Djillali Liabès de Sidi Bel-Abbès, Sidi Bel-Abbès 22000, Algeria
- ³ Laboratoire d'Elaboration et de Caractérisation des Matériaux (LECM), Université Djillali Liabès de Sidi Bel-Abbès, Sidi Bel-Abbès 22000, Algeria
- ⁴ Laboratoire de Physique Quantique de la Matière et de Modélisation Mathématique (LPQ3M), Université de Mascara, Mascara 29000, Algeria
- ⁵ Department of Physics and Astronomy, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia
- ⁶ Laboratory for Developing New Materials and Their Characterizations, Department of Physics, Faculty of Science, University of Ferhat Abbas-Setif 1, Setif 19000, Algeria
- ⁷ Department of Physics, College of Science, King Faisal University, P.O. Box 400, Al-Ahsa 31982, Saudi Arabia
- ⁸ College of Science, Physics Department, Alfaisal University, P.O. Box 50927, Riyadh 11533, Saudi Arabia
- * Correspondence: h_khachai@yahoo.fr (H.K.); khenata_rabah@yahoo.fr (R.K.); sosaid@alfaisal.edu (S.G.-S.)



Citation: Chiker, F.; Baki, N.; Khachai, Y.A.; Khachai, H.; Miloua, R.; Khenata, R.; Bin-Omran, S.; Bouhemadou, A.; Kanoun, M.B.; Goumri-Said, S. Spin-Polarized Study of the Structural, Optoelectronic, and Thermoelectric Properties of the Melilite-Type $\text{Gd}_2\text{Be}_2\text{GeO}_7$ Compound. *Crystals* **2022**, *12*, 1397. <https://doi.org/10.3390/cryst12101397>

Academic Editor: Konstanze R. Hahn

Received: 6 September 2022

Accepted: 27 September 2022

Published: 2 October 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Abstract: The present work is a theoretical study of the structural and spin-polarized dependent optoelectronic thermoelectric properties of the melilite-type $\text{Gd}_2\text{Be}_2\text{GeO}_7$ compound, using the full potential linearized augmented plane wave approach in the framework of density functional theory. The predicted structural parameters are in good accordance with the measured counterparts. It is found that the title compound is more stable in the ferromagnetic order than in the non-magnetic order. The calculated band structure using the modified Becke–Johnson potential reveals that the studied compound has a wide bandgap of 3.78 eV. The frequency-dependent linear optical spectra are studied in an energy range expanding from 0 to 30 eV. Finally, the semi classical Boltzmann theory as incorporated in the Boltztrap code is used to study the spin-polarized dependent transport properties. The obtained results show that $\text{Gd}_2\text{Be}_2\text{GeO}_7$ is a potential candidate for conversion energy device applications.

Keywords: magnetic semiconductors; complex oxide $\text{Gd}_2\text{Be}_2\text{GeO}_7$; spin-polarized DFT; optoelectronics; thin-film coating; thermoelectric properties

1. Introduction

Rare earth (RE melilite type $\text{RE}_2\text{Be}_2\text{GeO}_7$ compounds (RE = Pr, Nd, Gd, Yb, Dy) crystalize in a tetragonal structure with the $P4_21m$ space group. Yellow feldspar is a group of pyrosilicate compounds that may be found in high-temperature metamorphosed impure limestone and silica under soaked igneous rocks. [1–3]. They are employed in a variety of applications, including optical materials and fuel cell ingredients for the development of solid oxide fuel cell (SOFC) technology [4]. The 4f electrons in melilite compounds containing lanthanide atoms, in particular, are highly influenced by the surrounding coordination environment, and exhibit radically different behaviors compared with the single element. This structural characteristic has been widely used to create magnetic and optical materials with desired qualities [5,6]. Melilites have been a research focus for a long

time [7–9] because of the ability to combine and crystallize atoms to achieve entirely new usabilities and allow the discovery of a compound with a new function. This opportunity is one of the most important contributions that solid-state chemistry field makes to society. Warren [10] was the first to determine the crystal structure of a synthesized melilite. Many different melilite compounds have been produced since then [11–17].

One of such compounds, the $\text{Gd}_2\text{Be}_2\text{GeO}_7$ melilite type compound, has attracted attention; it was previously synthesized, and its crystal structure was characterized by Ochi et al. [18]. In addition, recently, Ashtaret et al. [19] reported the synthesis, structure, and magnetic properties of this compound and other families of melilite-type $\text{RE}_2\text{Be}_2\text{GeO}_7$ (RE = Pr, Nd, Dy, Yb) polycrystals using the solid-state reaction method. Few studies have highlighted the spin-polarized dependent optoelectronic and thermoelectric properties of melilite containing rare earth (RE) atoms which are considered to have a high degree of freedom of chemical composition. The discovery of new qualities resulting from the crystalline structure of the melilite-type compound was the focus of this research. The main goal of this study is to explain the spin-polarized contribution to the electronic band structure, optical response, and thermoelectric properties of $\text{Gd}_2\text{Be}_2\text{GeO}_7$ compound, using the FP-LAPW method based on density functional theory [20–25]. We find that the spin-polarized calculations with the modified Beck Johnson approach [26–29] raise the important wide-band gap magnetic semiconductor behavior in this compound.

This paper is organized as follows. A general introduction to the melilite compounds is given in Section 1. We summarize the significant parameters introduced in our theoretical methods used in this study in Section 2. In Section 3, we investigate the spin-polarized dependent calculations of the crystal structures, optoelectronics, and thermoelectric properties of $\text{Gd}_2\text{Be}_2\text{GeO}_7$ melilite-type compound. Furthermore, and in order to elucidate the optical coating properties, transmittance, reflectance, and absorbance at different thicknesses were performed. Concluding remarks are summarized in the last section.

2. Methodology and Calculation Settings

The full potential linear augmented plane wave (FP-LAPW) approach [22,23] based on density functional theory [20,21] as incorporated in the WIEN2k code [24] was used to investigate the structural, electronic, and magnetic characteristics of the melilite-type $\text{Gd}_2\text{Be}_2\text{GeO}_7$ compound. The GGA-PBE version of the generalized-gradient approximation (GGA) [25] and the modified Becke–Johnson potential by Tran and Blaha (TB-mBJ) [26–29] were used to treat the exchange-correlation effects. The muffin-tin sphere radius was chosen to be 1.8 Bohr for Gd and Ge, 1.4 Bohr for Be, and 1.35 Bohr for O. The energy convergence criterion was set to 10^{-4} Ry to ensure accurate computations. The electronic configuration of each element is taken as follows: Gd: $[\text{Xe}] 6s^2 4f^7 5d^1$, Be: $[\text{He}] 2s^2$, Ge: $[\text{Ar}] 4s^2 3d^{10} 4p^2$, and O: $[\text{He}] 2s^2 2p^4$. A dense Brillouin zone sampling of $18 \times 18 \times 28$ k-mesh was used for the optical and thermoelectric characteristics. The transport parameters were determined through the semi classical Boltzmann theory as implemented in the BoltzTrap code [30].

3. Results and discussion

3.1. Structural Properties

$\text{Gd}_2\text{Be}_2\text{GeO}_7$ is isostructural to the melilitetype group $\text{A}_2\text{MM}'_2\text{O}_7$, where A symbolizes bigger cations such as alkali earth ions and lanthanides, and M and M' denote smaller divalent to tetravalent cations. The melilite crystallizes in a tetragonal structure with space group $P\bar{4}2_1m$ (SG No13) [1–19], and can be represented as two-dimensional lattices in the ab-plane consisting of MO_4 and $\text{M}'\text{O}_4$ tetrahedra, with the larger A ions occupying the space between these lattices.

There are six crystallographic sites in the unit cell: one Wyckoff site 4e occupied by Gd atom, one site 2a occupied by Ge atom, one site 4e occupied by Be atom, and three Wyckoff sites 2c, 2a, 8f occupied by O atoms. Figure 1 depicts the crystal structure of melilite-type $\text{Gd}_2\text{Be}_2\text{GeO}_7$. Figure 2 shows that the title compound is more stable in the ferromagnetic order than in the non-magnetic one, so only the physical properties of $\text{Gd}_2\text{Be}_2\text{GeO}_7$ in

the ferromagnetic order were studied. The calculated total energy versus the volume data are fitted to the Birch–Murnaghan equation of state [31,32] and the obtained equilibrium structural parameters, such as the unit cell volume (V_0), lattice parameters (a , and c), bulk modulus (B_0) and its pressure derivative (B') are summarized in Table 1. We notice that our results are very close to the reported experimental data [18,19].

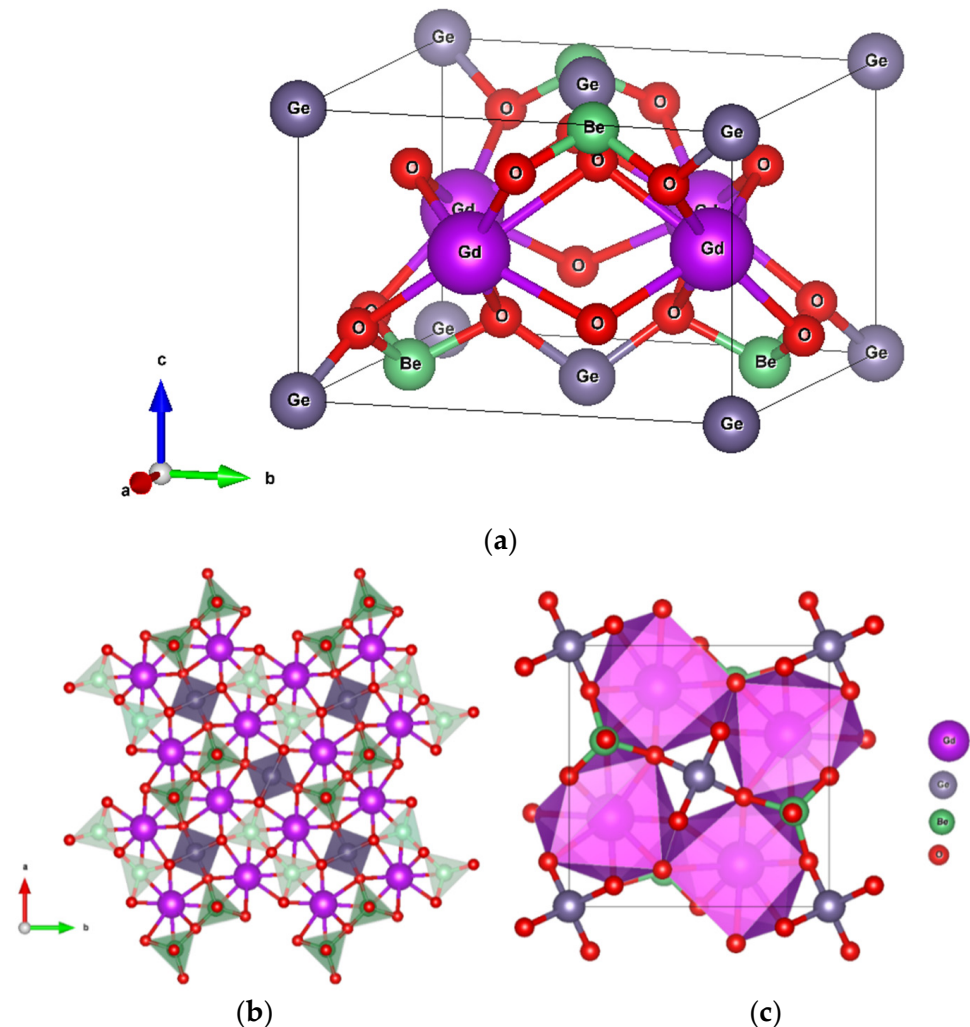


Figure 1. (a) The melilite crystalline structure of $Gd_2Be_2GeO_7$ compound, (b) connectivity of GdO_8 polyhedrons in the ab plane, and (c) c coordination environments of GdO_8 , BeO_4 , and GeO_4 polyhedron.

Table 1. Lattice constants a and c , bulk modulus B_0 , and its pressure derivative B' parameters optimization in both ferromagnetic (FM) and nonmagnetic orders (NM). For comparison, experimental and other theoretical values are included [18,19].

	a (Å)	c (Å)	V (Å ³)	B_0 (GPa)	B'	E_0 ($\times 10^6$ eV)	Reference	
$Gd_2Be_2GeO_7$	7.516	4.878	275.654	160.95	3.880	−1.371788	Present work	NM
	7.525	4.883	276.567	165.91	4.274	−1.371821	Present work	FM
	7.480	4.842	270.910	-	-	-	[18]	
	7.494	4.842	271.894	-	-	-	[19]	

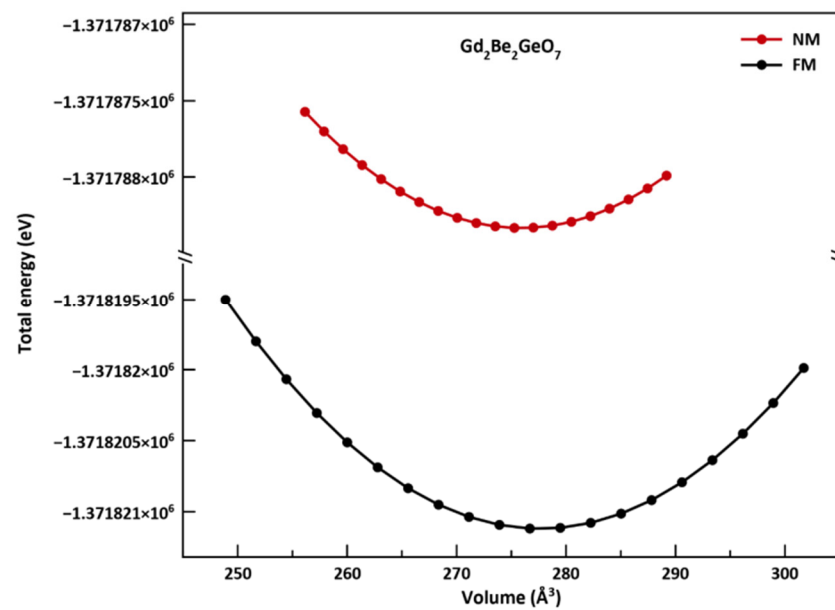


Figure 2. The total energy versus the volume for the ferromagnetic and non-magnetic $\text{Gd}_2\text{Be}_2\text{GeO}_7$ compound.

3.2. Electronic Properties

The electron energy band structure of the $\text{Gd}_2\text{Be}_2\text{GeO}_7$ compound was examined at equilibrium lattice parameters, taking into consideration spin polarization, based on the stable melilite phase; the computational procedure was accomplished using PBE-GGA and PBE-GGA-mBJ techniques. This allows us to go beyond traditional GGA/LSDA methodologies and treat electron correlations more accurately, correcting the band gap and the contribution of various orbitals. The Brillouin zone of the melilite structure is represented in Figure 3, with the recommended band path taken from reference [33].

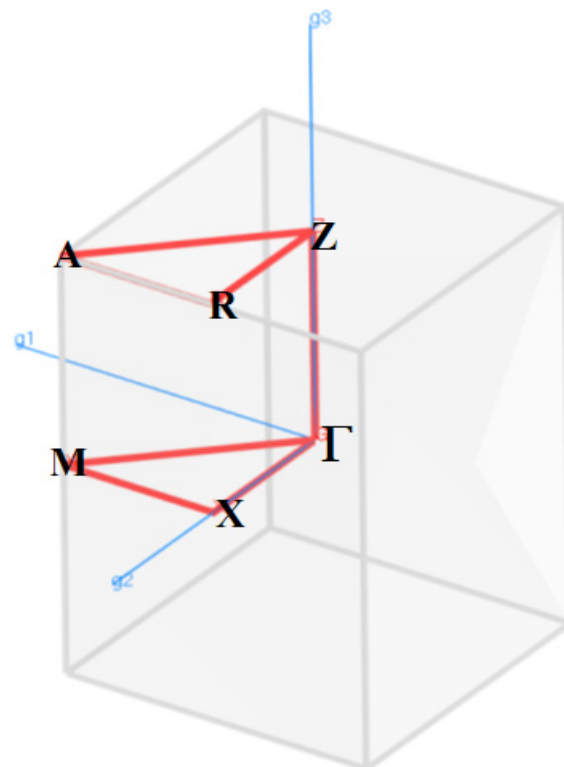


Figure 3. Brillouin zone of Tetragonal lattice. Path: Γ -X-M- Γ -Z-R-A-Z | X-R | M-A [33].

Including spin polarization with GGA-mBJ scheme, the calculated energy band dispersion and diagram of the total density of states (TDOS) of the $\text{Gd}_2\text{Be}_2\text{GeO}_7$ compound are illustrated in Figures 4 and 5, respectively, according to the spin-up and spin-down channels. Analysis of the obtained curves shows that this compound presents an interesting band gap behavior. First, as seen in Figure 4, the material under discussion exhibits an insulating band gap behavior with an indirect $\text{Z}-\Gamma$ band gap of 6.319 eV for the majority spin, while the semiconductor behavior of this compound predominates in the minority spin with a direct band gap $\text{Z}-\text{Z}$ of 3.928 eV in which the VBM is located below the Fermi level. Table 2 shows the computed values for the highest valence band (HVB) and lowest conduction band (LCB) in the tetragonal BZ for the examined $\text{Gd}_2\text{Be}_2\text{GeO}_7$ material at various high-symmetry k-points. Therefore, the spin-polarized $\text{Gd}_2\text{Be}_2\text{GeO}_7$ material has a direct wide-band gap ($Z_C - Z_V$) of about 3.781 eV. For the first time, these results are presented in the context of the DFT technique with the spin-polarized GGA-mBJ exchange potential for the best correction of the electronic band energies and their localizations. Figure 5 displays the atom projected density of states (PDOS) for those atomic species whose orbitals may have substantial contributions around the Fermi level, spin-up and spin-down polarizations to better understand the electronic and magnetic characteristics of $\text{Gd}_2\text{Be}_2\text{GeO}_7$. The energy levels below the Fermi level are mainly consisting of Ge-4s4p, Be-2s as well as the Gd-p states. The electronic states of Be and O atoms cohere with each other throughout the area from the VB to the CB, and the states of Ge and O atoms are likewise totally overlapped, indicating that these orbitals strongly hybridize with each other due to interactions in the BeO_4 and GeO_4 tetrahedrons.

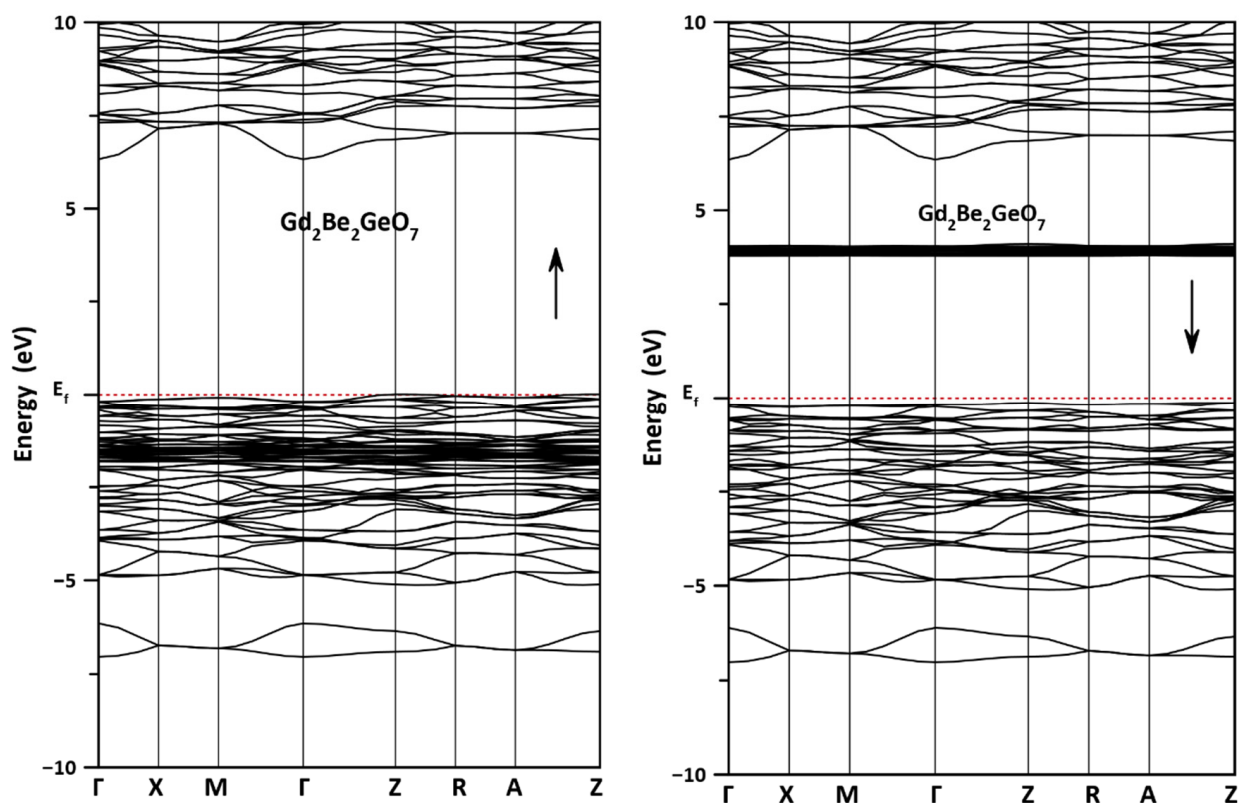


Figure 4. The spin-polarized electronic band structure for $\text{Gd}_2\text{Be}_2\text{GeO}_7$ compound in melilite tetragonal structure along with high symmetric directions with GGA-mBJ.

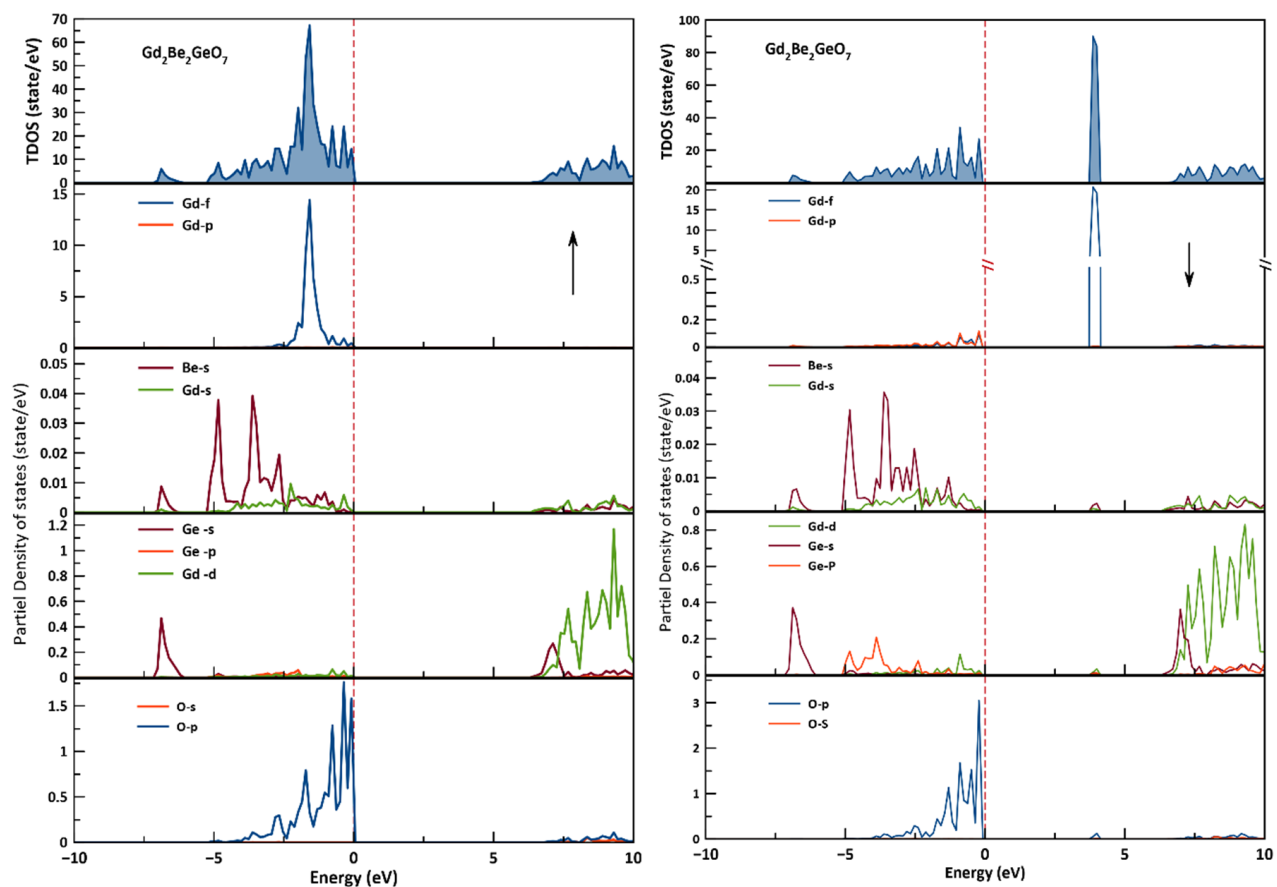


Figure 5. The spin- polarized total and orbital projected density of states (DOS) for $\text{Gd}_2\text{Be}_2\text{GeO}_7$ compound in melilite tetragonal structure using GGA + mBJ.

Table 2. The HVB and the LCB electron energies in eV (in the present work), evaluated with the GGA + mBJ exchange potential according to the majority spin (spin-up) and minority spin (spin-down) panels at different high-symmetry k-points for the $\text{Gd}_2\text{Be}_2\text{GeO}_7$ compound.

k-Points	Majority Spin (Spin-up)		Minority Spin (Spin-down)	
	HVB	LCB	HVB	LCB
Γ	−0.199	6.327	−0.183	3.792
X	−0.132	7.154	−0.246	3.792
M	−0.087	7.283	−0.212	3.796
Z	0.007	6.862	−0.139	3.788
R	−0.044	7.025	−0.191	3.79
A	−0.08	7.026	−0.164	3.803

In addition, the occupied f states of Gadolinium fall below the O-2p valence bands, spin-up (majority), whereas unoccupied f states of Gd fall in the band gap, spin-down (minority); finally the 5d-Gd are mainly localized in the conduction band both in majority spin (spin-up) and minority spin (spin-down) channels. The obtained values of the total magnetic moment (μ) of the studied compound $\text{Gd}_2\text{Be}_2\text{GeO}_7$ using spin-polarized GGA + mBJ calculations are observed around $7.497 \mu_B$, which agrees well with those found by Ochi. et al. [18] ($7.94\text{--}7.20 \mu_B$) and M. Ashtar et al. [19] ($7.05 \mu_B$). As seen in Table 3, most of the magnetic moments arise from the Gd-f states with small contributions from the interstitial region and the other constituent atoms.

Table 3. Calculated magnetic moments of each atom, interstitial, and cell for Gd₂Be₂GeO₇ compound in μ_B unit compared to experimental data.

	μ_{Inters}	μ_{Gd}	μ_{Be}	μ_{Ge}	μ_{O1}	μ_{O2}	μ_{O3}	$\mu_{\text{Tot}} (\mu_B)$
Gd ₂ Be ₂ GeO ₇	0.661	6.729	0.000	0.001	0.049	0.018	0.039	7.49 Present work 7.94–7.20 [18] 7.05 [19]

3.3. Optical Properties

Knowledge of the optical properties of materials is necessary before their implication in optoelectronic device applications. Therefore, an accurate theoretical method to assess the optical properties of materials is required. The state-of-the-art FP-LAPW method [24] with the GGA + mBJ functional [25,26] might be a good theoretical tool for the investigation of the optical properties of the melilite-type Gd₂Be₂GeO₇ compound. Furthermore, adding spin-polarized calculations to this method, the optical properties of this compound give interesting discussion and useful information about its internal structure [34,35].

The dielectric function $\varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2$ describes the linear response of a material to incident electromagnetic radiation, where ε_1 (the real part) describes the dispersion of radiation inside the medium and ε_2 (the imaginary part) describes the absorption of radiation by the medium [35,36]. All other optical coefficients, such as refractive indexes, reflectivity coefficient and absorption coefficient, can be calculated from the dielectric function through known relationships. Due to the tetragonal symmetry of the investigated material, all optical spectra are calculated for an electrical field vector E of the incident electromagnetic radiation polarized both parallel and perpendicular to the c -axis ($E//c$ and $E \perp c$).

Our findings serve as a prediction because no previous study on the optoelectronic properties of the title compound has been made. Figure 6 depicts the ε_2 spectrum for the Gd₂Be₂GeO₇ compound spin-up and spin-down channels in an energy range 0–30 eV. According to spin-polarized GGA + mBJ band structure computations, the compound under consideration's valence band maximum and conduction band minimum exhibit divergent behavior, where it can be an insulator for spin-up polarization and a semiconductor for spin-down polarization. The ε_2 spectra for both spin-up and spin-down channels clearly show the above characteristics. The absorption edge (the first critical point of $\varepsilon_2(\omega)$), occurring at 3.9 eV for the minority spin channel and at 6.319 eV for the majority spin channel, is originated from the electronic transitions from the valence band maximum states to the conduction band minimum states. The band structure has a significant impact on the optical metrics given above, and our findings are consistent with the specific electronic properties outlined in the preceding section.

The $\varepsilon_1(\omega)$ spectrum was calculated from that of $\varepsilon_2(\omega)$ through the Kramers-Kronig relation [37,38]. In spin-polarized optics computations, the Kramers-Kronig (KK) transformation is not a simple additive quantity [34]. The real and imaginary components of the dielectric function as a function of photon energy are shown in Figure 7. The absorptive component $\varepsilon_2(\omega)$ describes the optical transition process between the energy bands in materials. The optical spectra of materials are formed by the electronic transitions from the highest occupied orbitals in the valence band to the lowest vacant orbitals in the conduction band. The suitable optical transitions, according to the selection rules, are $s \rightarrow p$, $p \rightarrow d$, $d \rightarrow p$, $d \rightarrow f$, and so on. In the imaginary part $\varepsilon_2(\omega)$ curve, the threshold energy of the dielectric function occurs at $E_0 = 3.7$ eV, which corresponds to the fundamental gap at equilibrium.

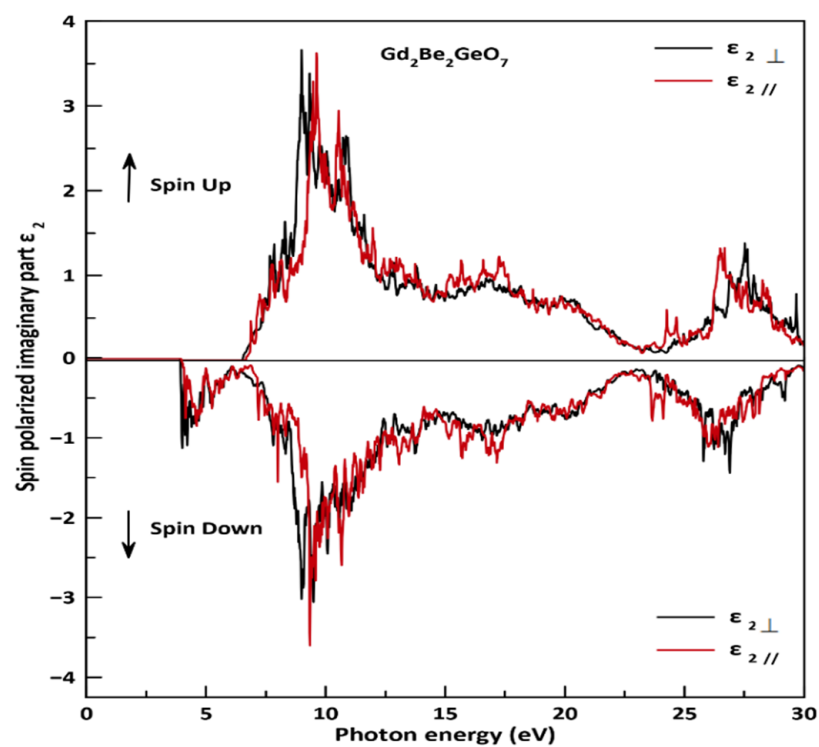


Figure 6. The spin- polarized optical calculations using GGA + mBJ for $\text{Gd}_2\text{Be}_2\text{GeO}_7$ compound.

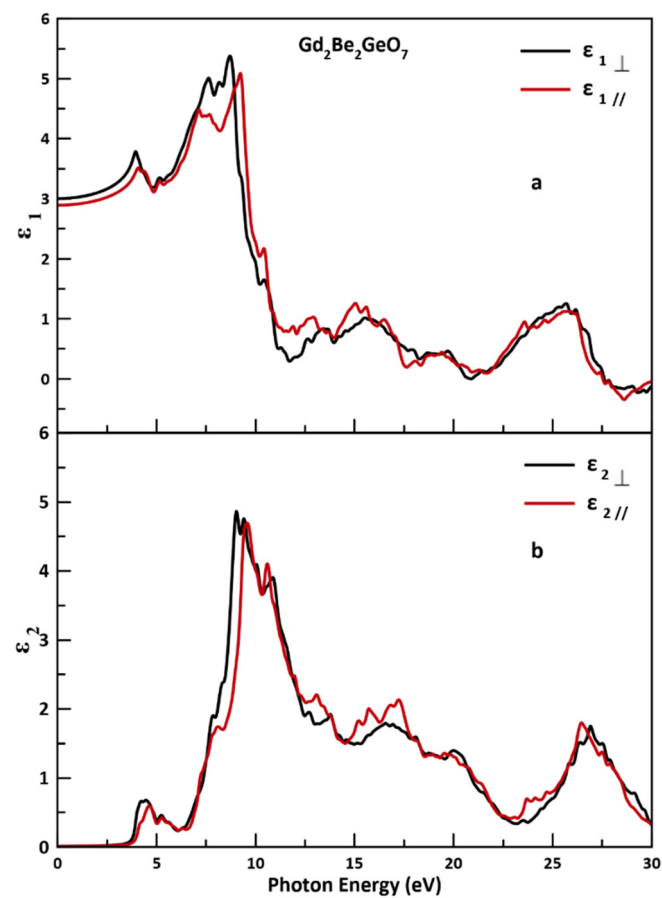


Figure 7. (a) The real part and (b) imaginary parts of the dielectric function in both parallel and perpendicular directions for $\text{Gd}_2\text{Be}_2\text{GeO}_7$ compound.

It is commonly accepted that materials with band gaps higher than 3.1 eV are suitable for uses in the ultraviolet (UV) spectrum. As a result, this broad band gap material might be appropriate for UV device applications. Furthermore, in the energy range of 7.5 to 17 eV, the $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ spectra exhibit a strong anisotropy in both directions of polarized light (parallel $E//c$ as well as perpendicular $E\perp c$ to the c -axis). This optical anisotropy is predicted due to the crystal's poor symmetry. The principal peaks of the $\epsilon_2(\omega)$ spectra are caused by electronic transitions from the O-p occupied valence states to the Gd-f and Gd-d empty conduction states.

Figure 7a shows $\epsilon_1(\omega)$ spectra. This function provides information about a material's electronic polarizability. The static dielectric constant $\epsilon_1(0)$ values for $E\perp c$ and $E//c$ are 3.002 and 2.893, respectively. $\epsilon_1(\omega)$ begins to increase from its zero frequency limit to reach a maximum value of 5.5 at 10 eV, and then drops below 0 on the negative scale for photon energy ranging from 26 to 28 eV. Figures 7b and 8b show a similar trend in the behavior of $\epsilon_2(\omega)$ and the extinction coefficient $k(\omega)$. The $k(\omega)$ threshold energy is roughly at 3.7 eV. At energies above this limit, $k(\omega)$ reaches its maximum value at 11 eV.

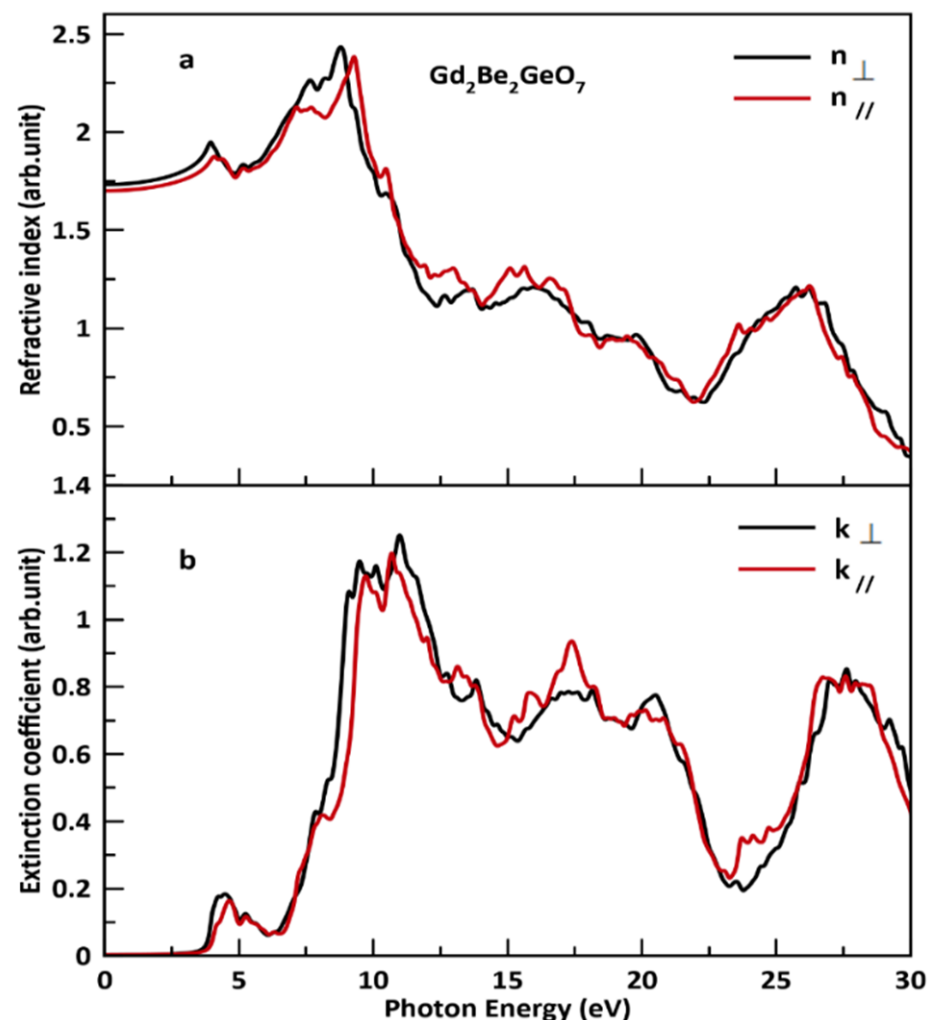


Figure 8. (a) Calculated refractive index $n(\omega)$ and (b) extinction coefficient $k(\omega)$ for $\text{Gd}_2\text{Be}_2\text{GeO}_7$ compound in both parallel and perpendicular directions.

At higher energy, both components of the extinction coefficient show a significant drop. The refractive index ($n(\omega)$) spectrum exhibits a noticeable anisotropy in the energy ranges 8–10 eV as can be seen in Figure 8a. The value of $n(\omega)$ becomes smaller than unity above 14 eV; this significant occurrence reflects the speed of light after passing through the substance. This effect could be beneficial in optoelectronics. The static refractive indices $n_{\perp}(0)$ and

$n_{||}(0)$ are 1.732 and 1.701, respectively, and the corresponding birefringence $\Delta n(0)$ is 0.031. The absorption of photons of light determines the excitation energy of an electron for passing over the band gap of a material. $\varepsilon_2(\omega)$ is directly related to the absorption coefficient $\alpha(\omega)$, which is defined as the amount of power absorbed when light passes through a solid. The optical absorption spectra of the described compound, as shown in Figure 9, demonstrate that it has a relatively high optical absorption ($>150 \text{ cm}^{-1}$) throughout a large energy range in the ultraviolet range between 5 and 20 eV. Furthermore, the absorption coefficient $\alpha(\omega)$ has peaked at 8 eV, 10 eV and 12 eV, which correspond to the inter-band transitions and then it gradually takes the higher values at higher photon energies. Despite the fact that the discussed compound ($\text{Gd}_2\text{Be}_2\text{GeO}_7$) has a wide-band gap and is structurally anisotropic; in lower photon energy region it is found to be optically isotropic, for which this feature makes it a potential candidate for the scintillator applications.

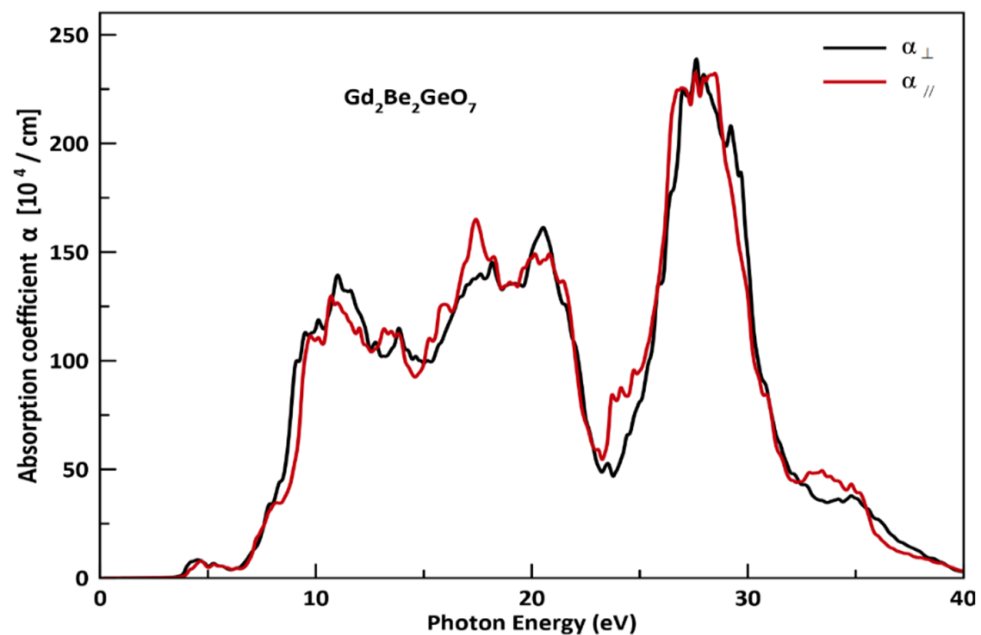


Figure 9. For the $\text{Gd}_2\text{Be}_2\text{GeO}_7$ compound, the absorption coefficient $\alpha(\omega)$ was calculated in both parallel and perpendicular orientations.

3.4. Optical Coating Characteristics

We attempted to examine the layer coating of the melilite-type compound $\text{Gd}_2\text{Be}_2\text{GeO}_7$ using the optical matrix approach, which is crucial for optical thin film design programs [39,40], in order to characterize the optical properties of this material to this extent.

This method considers each layer of the material as a 2×2 matrix, with the previously calculated extinction coefficient and refractive index of the optical properties (Section 3.3), resulting in thin films optical properties such as transmittance, absorbance, and reflectance, which are functions of the extinction coefficient (k) and refractive index (n), as well as geometry (thickness (d), surface roughness), etc. [41–46]. Two techniques were used in the optical cladding research: one on a clear substrate ($n_{\text{glass}} = 1.5$, $k_{\text{glass}} = 0$) and the other on a free-standing layer ($n_{\text{air}} = 1$, $k_{\text{air}} = 0$). Figures 10–12 show plots of optical coating spectra of the examined $\text{Gd}_2\text{Be}_2\text{GeO}_7$ thin film, such as Transmittance, Absorbance, and Reflectance, in the wavelength range of 150–1200 nm, for five different thicknesses: 100 nm, 300 nm, 600 nm, 1000 nm, and 1300 nm, respectively.

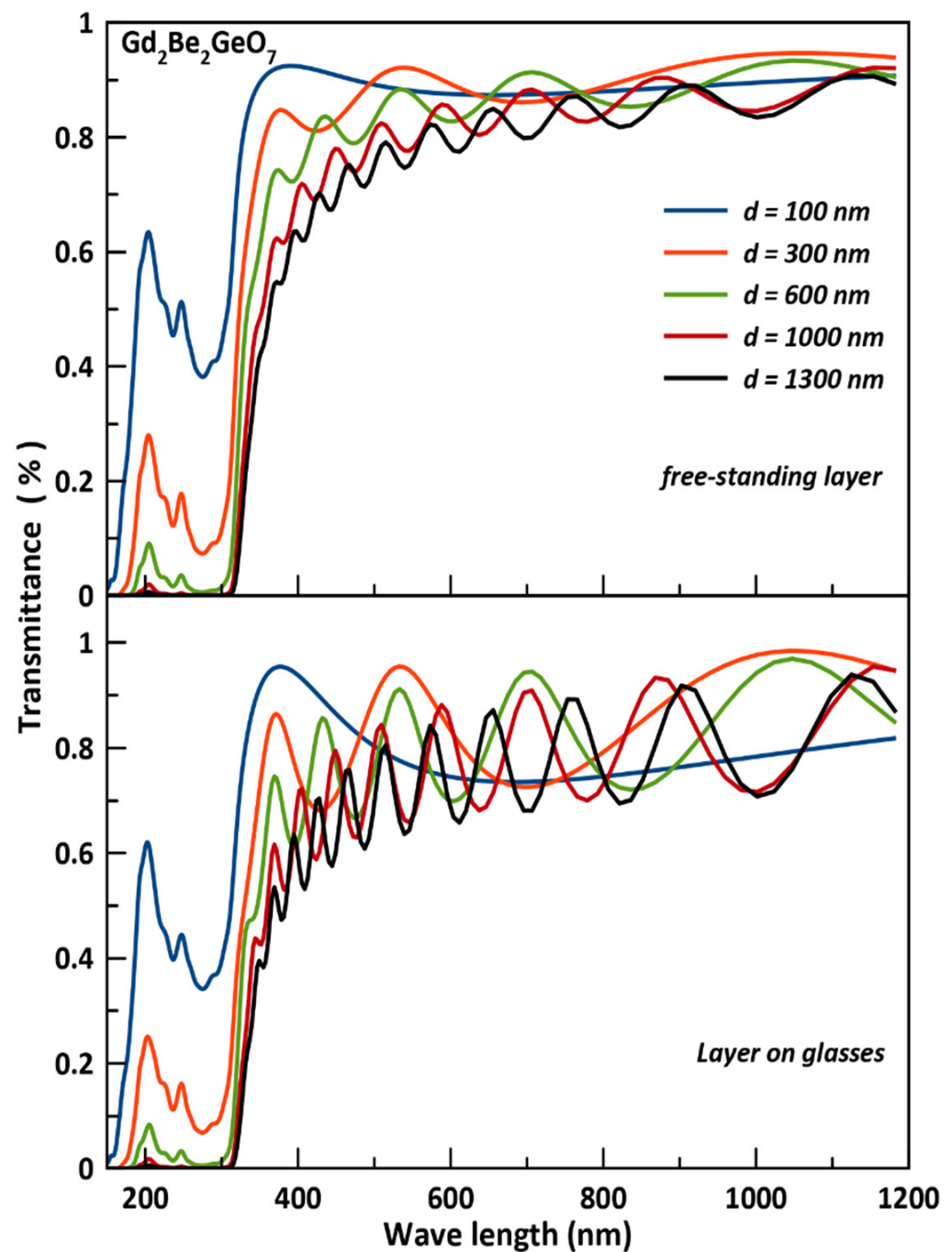


Figure 10. The transmittance spectra for $\text{Gd}_2\text{Be}_2\text{GeO}_7$ thin films employing varying thicknesses in both processes of coating (free-standing layer and layer mounted on glasses).

One can see from the plots of transmittance (Figure 10) that the $\text{Gd}_2\text{Be}_2\text{GeO}_7$ thin film exhibits a good transparency (between 90% and 95%) in the visible and infrared regions, and with increasing thickness, transmittance spectra diminish slowly at a higher wavelength level. Furthermore, the transmittance spectrum achieves the perfect shape for a sample of 100 nm thickness. Where for $\text{Gd}_2\text{Be}_2\text{GeO}_7$ thin film on transparent substrate, the maximum value of transmittance was found to be 92% at wavelengths around 350–450 nm and keeping this magnitude at a higher wavelength range, whereas the transmittance of 95% at wavelengths around 400 nm is found in the case of free-standing layers of this thin film and then decreases at higher wavelengths. Figure 11 shows the absorbance spectra of the $\text{Gd}_2\text{Be}_2\text{GeO}_7$ thin film under consideration. The plots show that the magnitude of this thin film's absorbance increases with the gradual increase in film thickness due to

an increase in the thin film's absorbance for both cases of the investigated coating steps (free-standing layer and on transparent substrate), especially in the UV-visible spectrum (200–750 nm).

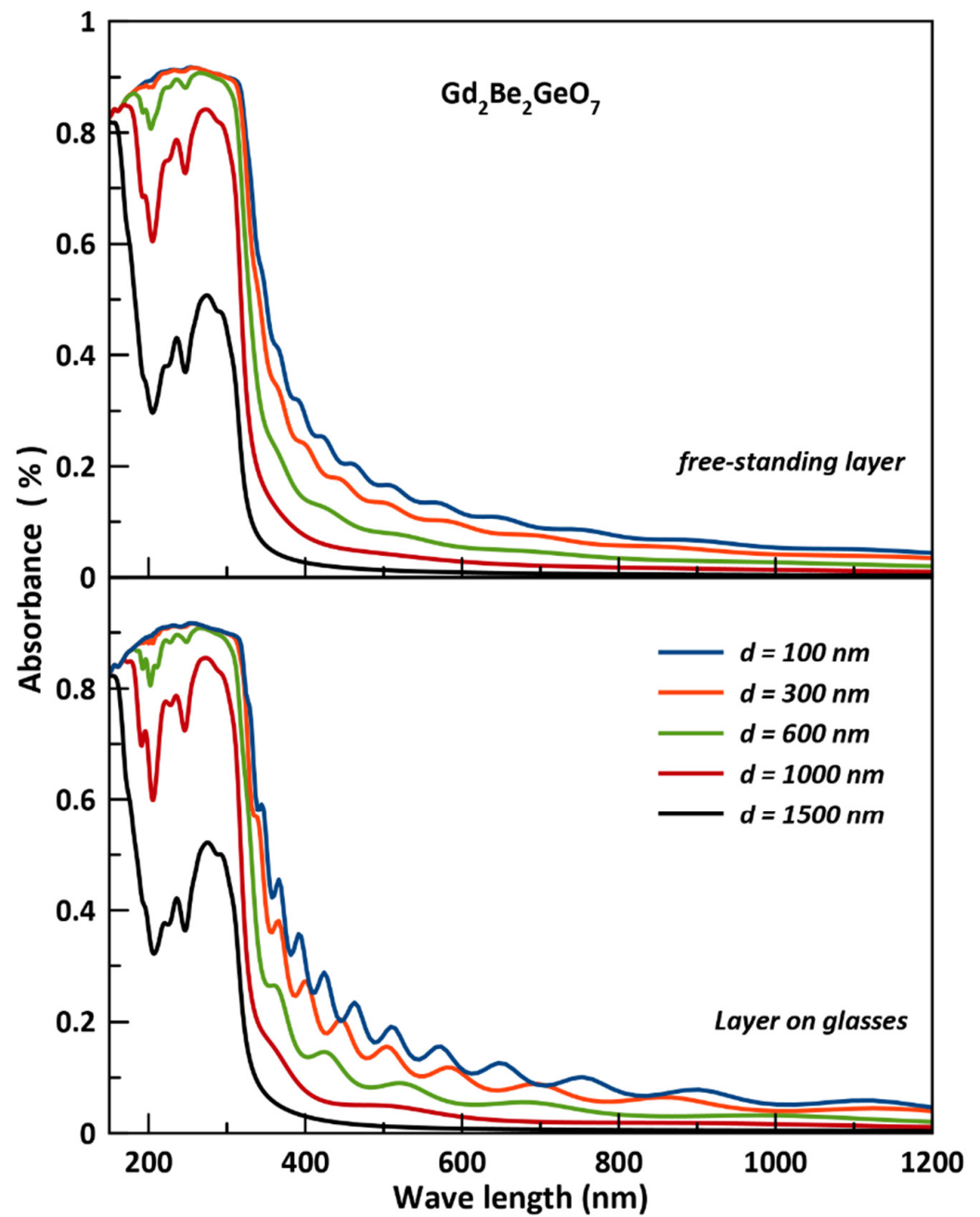


Figure 11. Absorbance spectra for $\text{Gd}_2\text{Be}_2\text{GeO}_7$ thin films with various thicknesses in both coating processes (free-standing layer and layer supported on glasses).

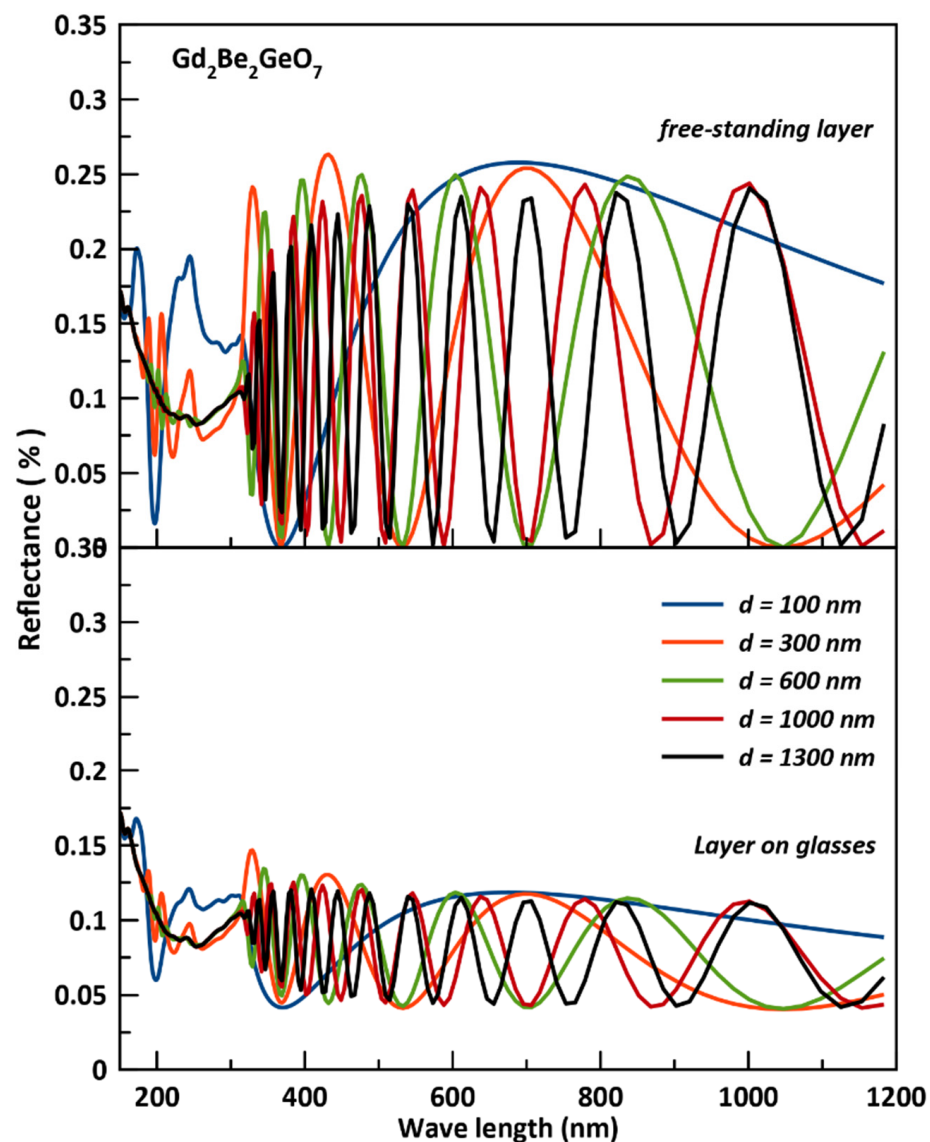


Figure 12. The reflectance spectra of $\text{Gd}_2\text{Be}_2\text{GeO}_7$ thin films with various thicknesses in both coating processes (free-standing layer and layer supported on glasses).

The absorbance peaks were found in the range of 200 nm to 300 nm as shown in Figure 11, for which we can conclude that the studied $\text{Gd}_2\text{Be}_2\text{GeO}_7$ thin film can be more efficient for applications in the ultraviolet (UV) region of the spectrum, and it could be useful for the high frequency UV device applications. Another important remark is that this thin film for very thin thicknesses of 100 nm can have good transparency in the visible spectrum (400–700 nm), which makes it a suitable candidate for optical coating design devices.

Figure 12 shows the computed optical reflectance spectra of our thin film under discussion for various layer thicknesses ($d = 100$ nm to $d = 1300$ nm) and both scenarios of the investigated coating steps: free-standing layer and transparent substrate. When moving from a free-standing layer to a layer on a glassy substrate, the form of the reflectance spectra changes dramatically. As a result, the usage of a glass substrate has an effect on the amplitude of interference oscillations. The interference phenomenon generated by the relative difference in refractive indices and thicknesses between the substrate and the film causes these rhythmic behaviors.

3.5. Thermoelectric Properties

In addition to detailed optoelectronic descriptions given obviously for the melilite-type $\text{Gd}_2\text{Be}_2\text{GeO}_7$ compound, in this subsection, we extended our investigation to explore its thermoelectric properties in order to study its ability to convert waste heat into useful electricity. The efficiency of thermoelectric power generation, on the other hand, is assessed by a dimensionless parameter called figure of merit (ZT), which is given as $ZT = S^2\sigma T/(\kappa_e + \kappa_L)$, where S is the Seebeck coefficient, T is the absolute temperature, and κ_e and κ_L are the material's electronic and lattice thermal conductivities, respectively [47–53]. We used the BoltzTraP code [30] with a mesh of $18 \times 18 \times 28$ k-points for this purpose. Variation of the Seebeck coefficient as a function of temperature of intrinsic (pure) $\text{Gd}_2\text{Be}_2\text{GeO}_7$ material is presented for the chemical potential $\mu = 0$, which is in the middle of the band gap for spin-up and spin-down channels (see Figure 13a). The behavior of the Seebeck coefficient was relatively similar in the two spin channels, even though we stated different values, but the variation with temperature demonstrated a declining tendency in both spin-up and spin-down channels, respectively, from a very high value of $\sim 270 \mu\text{V/K}$ and $\sim 1700 \mu\text{V/K}$. The Seebeck coefficients in both spin channels are positive, indicating that the holes are substantially dominating in this material.

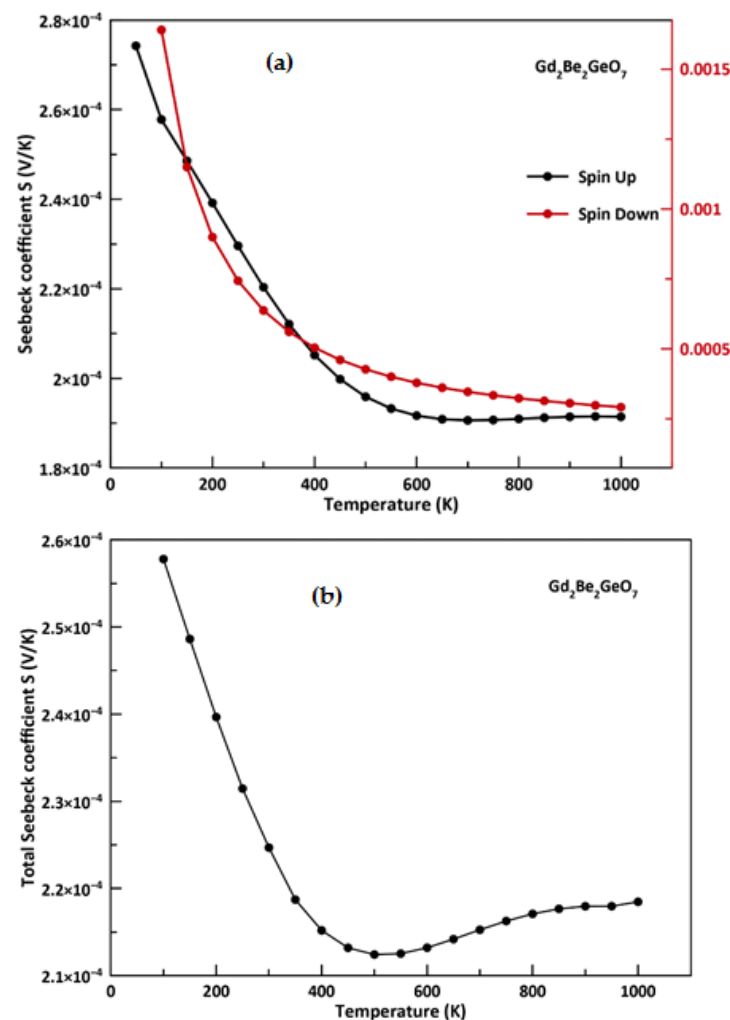


Figure 13. (a) Calculated total Seebeck coefficient (S) as a function of temperature for $\text{Gd}_2\text{Be}_2\text{GeO}_7$ compound in both spin channels (up and down); (b) Calculated total Seebeck coefficient (S) as a function of temperature for $\text{Gd}_2\text{Be}_2\text{GeO}_7$ compound.

Furthermore, we calculated the absolute Seebeck coefficient given by the following formula [47–53]:

$$S_{\text{tot}} = \frac{\sigma(\uparrow)S(\uparrow) + \sigma(\downarrow)S(\downarrow)}{\sigma(\uparrow) + \sigma(\downarrow)}$$

The Seebeck coefficient is plotted as a function of temperature in Figure 13b, and it was positive throughout the temperature range for the examined compound, implying that holes are the charge carriers and that the spin-down state dominates the spin-up state. The presence of a low carrier concentration is indicated by the sharply higher values of the computed total S at lower temperatures <300 K. It has a value of $224.68 \mu\text{V/K}$ at room temperature, and we see a little drop in the total Seebeck value at higher temperatures. As a result, the computed Seebeck coefficients of $\text{Gd}_2\text{Be}_2\text{GeO}_7$ compound in this study make it a promising material for thermoelectric devices.

To make a good thermoelectric device, the TE material used should have a high S , as well as high σ and low $k = \kappa_e + \kappa_L$ at the same time [47–53]. The results of temperature dependence of the electronic thermal conductivity ($\kappa_{\text{el}}(\text{W/K}\cdot\text{m})$) for the two spin channels are shown in Figure 14 for the considered compound. We can clearly see that the κ_{el} after saturated values at low temperatures starts to increase rapidly with increasing temperature for the two spin channels (down and up). The κ_{el} values at room temperature are $1.984 \times 10^{12} \text{ W/K}\cdot\text{m}$ and $2.718 \times 10^{13} \text{ W/K}\cdot\text{m}$ for spin-down and spin-up channels, respectively. One can state that the compound under discussion shows important thermal behavior near room temperature where the thermal conductivity has lower values and higher Seebeck coefficient as expected, as shown in Figures 13b and 14.

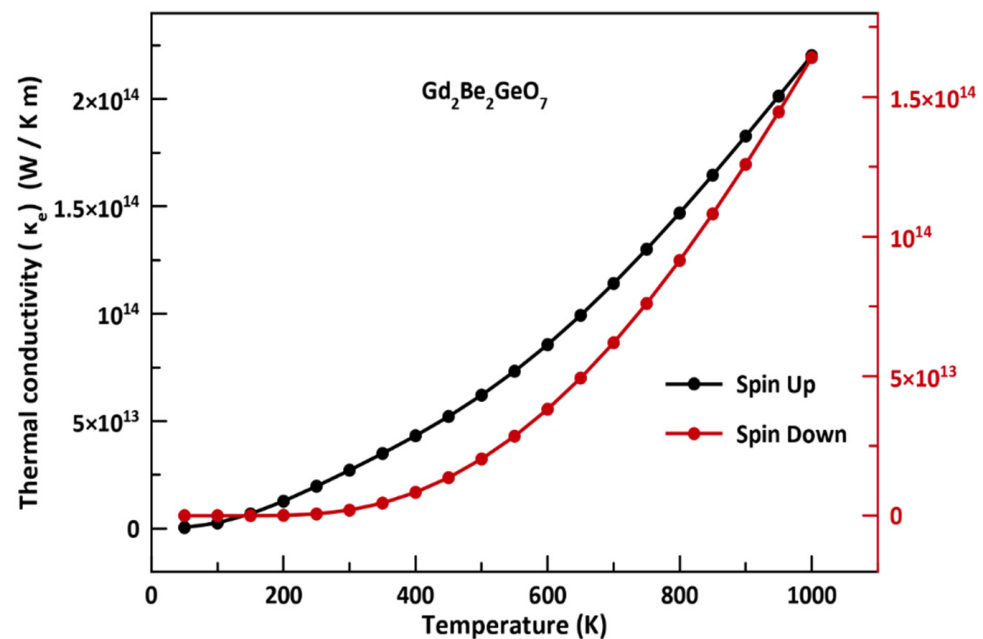


Figure 14. Calculated thermal conductivity κ_{el}/τ as a function of temperature in both spin channels (up and down) for $\text{Gd}_2\text{Be}_2\text{GeO}_7$ compound.

The higher the ZT value, the higher the thermoelectric conversion efficiency. The variation of ZT with temperature is shown in Figure 15 for the compound under discussion for the spin channels. Our results show that reasonable performance associated with ZT values around 1 is probably likely for the minority spin channel, particularly at 100K. Furthermore, it can be clearly seen that the ZT value decreases gradually with increasing temperature, while, for the majority spin channel, ZT reaches a value of about 0.89 at low temperature and then starts to decrease with increasing temperature. Higher values of ZT (approximately 0.99 and 0.70) for a large temperature range indicate that the examined compound has good thermoelectric performance and could be a suitable material for

thermoelectric generator applications. The mobility of free charge carriers causes an electrical conductivity (σ/τ) in transport properties, which is a key component that must be high for desired thermoelectric materials to lower the Joule heating effect [47–54]. Figure 16 shows the predicted electrical conductivity (σ/τ) of the $\text{Gd}_2\text{Be}_2\text{GeO}_7$ compound as a function of temperature for both spins (up and down) configurations. The material exhibits approximately the same behavior in both channel configurations and σ/τ increases at given temperatures showing semiconductor behavior. Despite that, in the case of spin-down channel the value of σ/τ remains constant at low temperatures but above 300 K, a strong variation of σ/τ is observed with temperature.

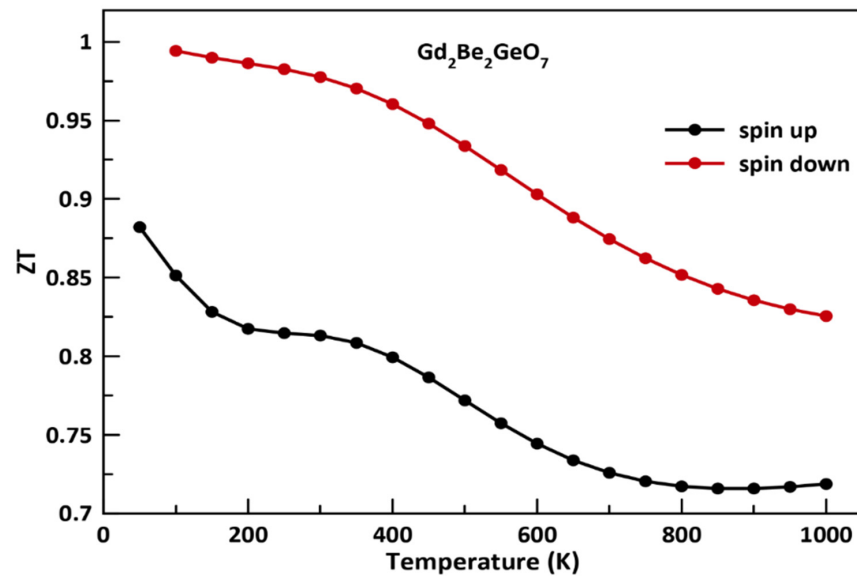


Figure 15. Figure of merit (ZT) for $\text{Gd}_2\text{Be}_2\text{GeO}_7$ compound as a function of temperature in both spin channels (up and down).

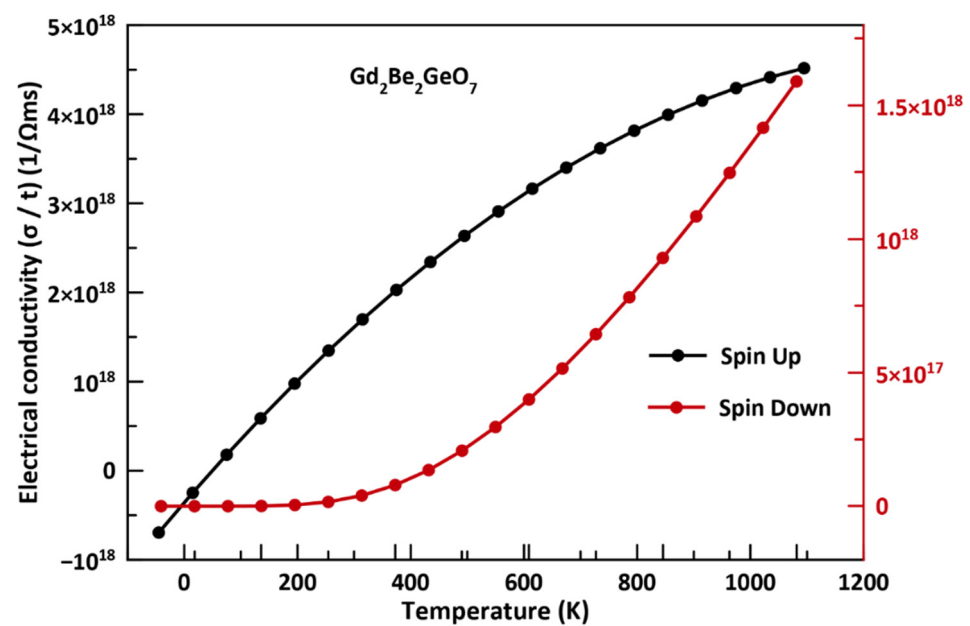


Figure 16. Variation of electrical conductivity (σ/τ) in both spin channels (up and down) as a function of temperature for $\text{Gd}_2\text{Be}_2\text{GeO}_7$ compound.

The reported value of electrical conductivity at ambient temperature is $1.69 \times 10^{18} (\Omega \text{ m s})^{-1}$, which increases to $4.51 \times 10^{18} (\Omega \text{ m s})^{-1}$ around 1000 K in the spin-up channel. The value of the spin-down channel, on the other hand, climbs dramatically from $1.59 \times 10^{16} (\Omega \text{ m s})^{-1}$

at room temperature to $1.58 \times 10^{18} (\Omega \text{ m s})^{-1}$ at 1000 K. When compared to the spin-down arrangement, the electrical conductivity of the spin-up configuration is higher.

4. Conclusions

The structural, optoelectronics, and transport characteristics of the melilite-type $\text{Gd}_2\text{Be}_2\text{GeO}_7$ compound have been investigated using the FP-LAPW method with the GGA-PBE and TB-mBJ functionals. From the obtained results, the important following conclusions can be drawn:

- The calculated lattice constants agree well with the available experimental data.
- The studied $\text{Gd}_2\text{Be}_2\text{GeO}_7$ as thin film could be a good transparent in the visible spectrum (400–700 nm) for very thin thickness of 100 nm which makes it a suitable candidate for optical coating design devices; furthermore, it can be more efficient for applications in the ultraviolet (UV) region of the spectrum, and it could be useful for the high frequency UV device applications regarding the high absorbance peaks found in the range of 200 nm to 300 nm.
- From spin-polarized thermoelectric calculations, the material under discussion presents adequate Seebeck coefficients around room temperature; furthermore, we found higher values of the figure of merit (around 0.99 and 0.70) over large temperature ranges which suggest that this material exhibits good thermoelectric performance and it could be a promising material for applications in thermoelectric generators.
- Finally, the electrical conductivity (σ/τ) as a function of temperature exhibits the behavior of a typical semiconductor.

Author Contributions: Conceptualization, F.C., N.B., Y.A.K., H.K., R.M., R.K., A.B., M.B.K. and S.G.-S.; methodology, F.C., N.B. and Y.A.K.; software, F.C., N.B., Y.A.K., R.K., M.B.K. and S.G.-S.; validation, F.C., N.B., Y.A.K., H.K., R.M., R.K., A.B., M.B.K. and S.G.-S.; formal analysis, F.C., N.B., Y.A.K., H.K., R.M., R.K., A.B., M.B.K. and S.G.-S.; investigation, F.C., N.B., Y.A.K., H.K., R.M., R.K., A.B., M.B.K. and S.G.-S.; resources, F.C., N.B., Y.A.K., H.K., R.M., R.K., A.B., S.B.-O., M.B.K. and S.G.-S.; data curation, F.C., N.B., Y.A.K., H.K., R.M., R.K., A.B., M.B.K. and S.G.-S.; writing—original draft preparation, F.C., N.B., Y.A.K., H.K., R.M., R.K., A.B., M.B.K. and S.G.-S.; writing—review and editing, F.C., N.B., Y.A.K., H.K., R.M., R.K., A.B., M.B.K. and S.G.-S.; visualization, F.C., N.B. and Y.A.K.; supervision, F.C., N.B., Y.A.K. S.B.-O. and S.G.-S.. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data used to support the findings of this study are available from the corresponding authors upon request.

Acknowledgments: The author F.C. acknowledge the financial Supporting Project number (B00L02UN220120220001), of the General Direction of Scientific Research and Technological Development (DGRSDT). The author S.B.-O. acknowledges Researchers Supporting Project number (RSP-2021/82), King Saud University, Riyadh, Saudi Arabia. Author S.G.-S. thanks Alfaisal University Research Office for supporting her research with internal research grant 22413.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Nurse, R.W.; Midgley, H.G. The system $\text{CaO}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$. *J. Iron Steel Inst.* **1953**, *174*, 121.
2. Burzo, E. Melilites and related silicates. In *Sorosilicates*; Springer: Berlin/Heidelberg, Germany, 2009; Volume 14, pp. 29–60.
3. Louisnathan, S.J. Refinement of the crystal structure of a natural gehlenite, $\text{Ca}_2\text{Al}(\text{Al}, \text{Si})_2\text{O}_7$. *Can. Mineral.* **1971**, *10*, 822–837.
4. Kuang, X.; Green, M.A.; Niu, H.; Zajdel, P.; Dickinson, C.; Claridge, J.B.; Jantsky, L.; Rosseinsky, M.J. Interstitial oxide ion conductivity in the layered tetrahedral network melilite structure. *Nat. Mater.* **2008**, *7*, 498–504. [[CrossRef](#)] [[PubMed](#)]
5. Xia, Z.; Liu, Q. Progress in discovery and structural design of color conversion phosphors for LEDs. *Prog. Mater. Sci.* **2016**, *84*, 59–117. [[CrossRef](#)]

6. Xia, Z.; Ma, C.; Molokeev, M.S.; Liu, Q.; Rickert, K.; Poeppelmeier, K.R. Chemical Unit Cosubstitution and Tuning of Photoluminescence in the $\text{Ca}_2(\text{Al}_{1-x}\text{Mg}_x)(\text{Al}_{1-x}\text{Si}_{1+x})\text{O}_7:\text{Eu}^{2+}$ Phosphor. *J. Am. Chem. Soc.* **2015**, *137*, 12494–12497. [CrossRef]
7. Louisnathan, S.J. Refinement of the crystal structure of hardystonite, $\text{Ca}_2\text{ZnSi}_2\text{O}_7$. *Z. Krist. Cryst. Mater.* **1969**, *130*, 427. [CrossRef]
8. Weiss, J.; Rosenstein, G. Addition of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ to manganese-doped barium titanate: Effect on oxygen diffusion and grain-boundary composition. *J. Mater. Sci.* **1988**, *23*, 3263–3271. [CrossRef]
9. Peng, C.; Tsao, R.; Chou, Z. Gugiaite, $\text{Ca}_2\text{BeSi}_2\text{O}_7$, a new beryllium mineral and its relation to the melilite group. *Sci. Sin.* **1962**, *11*, 977–988.
10. Warren, B.E. The structure of melilite $(\text{Ca},\text{Na})_2(\text{Mg},\text{Al})_1(\text{Si},\text{Al})_2\text{O}_7$. *Z. Kristallogr.* **1930**, *74*, 131–138. [CrossRef]
11. Ben Yahia, H.; Essehli, R.; Belharouak, I.; Gaudin, E. Crystal structure and magnetic properties of $\text{K}_2\text{CoV}_2\text{O}_7$. *Mater. Res. Bull.* **2015**, *71*, 7–10. [CrossRef]
12. Matsubara, S.; Miyawaki, R.; Kato, A.; Yokoyama, K.; Okamoto, A. Okayamalite, $\text{Ca}_2\text{B}_2\text{SiO}_7$, a new mineral, boron analogue of gehlenite. *Mineral. Mag.* **1998**, *62*, 703–706. [CrossRef]
13. Akasaka, M.; Ohashi, H. ^{57}Fe mössbauer study of synthetic Fe^{3+} -melilites. *Phys. Chem. Miner.* **1985**, *12*, 13–18. [CrossRef]
14. Smith, J.V. Reexamination of the crystal structure of melilite. *Amer. Miner.* **1953**, *38*, 643–661.
15. Smith, J.V. X-ray-emission microanalysis of rock-forming minerals. I. Experimental techniques. *J. Geol.* **1965**, *73*, 830–864. [CrossRef]
16. Tyutyunnik, A.P.; Zubkov, V.G.; Surat, L.L.; Slobodin, B.V.; Svensson, G. Synthesis and crystal structure of the pyrovanadate $\text{Na}_2\text{ZnV}_2\text{O}_7$. *Powder Diffr.* **2005**, *20*, 189–192. [CrossRef]
17. Kloss, S.D.; Weidmann, N.; Niklaus, R.; Schnick, W. High-Pressure Synthesis of Melilite-type Rare-Earth Nitridophosphates $\text{RE}_2\text{P}_3\text{N}_7$ and a $\text{Ba}_2\text{Cu}[\text{Si}_2\text{O}_7]$ -type Polymorph. *Inorg. Chem.* **2016**, *55*, 9400–9409. [CrossRef] [PubMed]
18. Ochi, Y.; Morikawa, H.; Minato, I.; Marumo, F. Preparation and magnetic property of new rare earth compounds $\text{R}_2\text{GeBe}_2\text{O}_7$ ($\text{R} = \text{La}, \text{Pr}, \text{Sm}, \text{Gd}, \text{Dy}, \text{Er}$) and $\text{Y}_2\text{GeBe}_2\text{O}_7$. *Mat. Res. Bull.* **1982**, *17*, 911–916. [CrossRef]
19. Ashtar, M.; Bai, Y.; Xu, L.; Wan, Z.; Wei, Z.; Liu, Y.; Marwat, M.A.; Tian, Z. Structure and Magnetic Properties of Melilite-Type Compounds $\text{RE}_2\text{Be}_2\text{GeO}_7$ ($\text{RE} = \text{Pr}, \text{Nd}, \text{Gd}-\text{Yb}$) with Rare-Earth Ions on Shastri–Sutherland Lattice. *Inorg. Chem.* **2021**, *60*, 3626–3634. [CrossRef]
20. Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* **1964**, *136*, B864–B871. [CrossRef]
21. Kohn, W.; Sham, L.J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, A1133–A1138. [CrossRef]
22. Andersen, O.K. Linear methods in band theory. *Phys. Rev. B.* **1975**, *12*, 3060–3083. [CrossRef]
23. Singh, D.J. *Plane Waves, Pseudopotentials and the LAPW Method*; Kluwer Academic: Dordrecht, The Netherlands, 1994.
24. Schwarz, K.; Blaha, P.; Madsen, G.K.; Kvasnicka, D.; Luitz, J. *An Augmented Plane Waves + Local Orbital Program for calculating Crystal Properties*; Institut Für Physikalische und Theoretische Chemie: Vienna, Austria, 2001.
25. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865. [CrossRef] [PubMed]
26. Becke, A.D.; Johnson, E.R. A simple effective potential for exchange. *J. Chem. Phys.* **2006**, *124*, 221101. [CrossRef] [PubMed]
27. Tran, F.; Blaha, P. Accurate Band Gaps of Semiconductors and Insulators with a Semilocal Exchange-Correlation Potential. *Phys. Rev. Lett.* **2009**, *102*, 226401. [CrossRef] [PubMed]
28. Koller, D.; Tran, F.; Blaha, P. Merits and limits of the modified Becke-Johnson exchange potential. *Phys. Rev. B* **2011**, *83*, 195134. [CrossRef]
29. Koller, D.; Tran, F.; Blaha, P. Improving the modified Becke-Johnson exchange potential. *Phys. Rev. B* **2012**, *85*, 155109. [CrossRef]
30. Madsen, G.K.; Singh, D.J. BoltzTraP. A code for calculating band-structure dependent quantities. *Comput. Phys. Commun.* **2006**, *175*, 67–71. [CrossRef]
31. Murnaghan, F.D. The Compressibility of Media under Extreme Pressures. *Proc. Natl. Acad. Sci. USA* **1944**, *30*, 244. [CrossRef]
32. Birch, F. Finite Elastic Strain of Cubic Crystals. *Phys. Rev.* **1947**, *71*, 809. [CrossRef]
33. Available online: <https://materialsproject.org/materials/mp-650715?chemsys=Gd-Be-Ge-O> (accessed on 17 August 2022).
34. Ambrosch-Draxl, C.; Sofo, J.O. Linear optical properties of solids within the full-potential linearized augmented planewave method. *Comput. Phys. Commun.* **2006**, *175*, 1–14. [CrossRef]
35. Amin, B.; Ahmad, I.; Maqbool, M.; Goumri-Said, S.; Ahmad, R. Ab initio study of the bandgap engineering of $\text{Al}_{1-x}\text{Ga}_x\text{N}$ for optoelectronic applications. *J. Appl. Phys.* **2011**, *109*, 023109. [CrossRef]
36. Bassani, F.; Parravicini, G.P.; Ballinger, R.A.; Birman, J.L. *Electronic States and Optical Transitions in Solids*; Pergamon Press: Oxford, UK, 1973.
37. Kramers, H.A. *Collected Science Papers*; North Holland: Amsterdam, The Netherlands, 1956.
38. Kronig, R.D.L. On the Theory of Dispersion of X-Rays. *J. Opt. Soc. Am.* **1926**, *12*, 547. [CrossRef]
39. Macleod, H.A. *Thin Film Optical Filters*, 2nd ed.; Adam Hilger: Bristol, UK, 1986.
40. Born, M.; Wolf, E. *Principles of Optics*, 3rd ed.; Pergamon: Oxford, UK, 1965.
41. Derkaoui, Z.; Kebbab, Z.; Miloua, R.; Benramdane, N. Theoretical study of optical characteristics of multilayer coatings $\text{ZnO}/\text{CdS}/\text{CdTe}$ using first-principles calculations. *Solid State Commun.* **2009**, *149*, 1231–1235. [CrossRef]
42. Miloua, R.; Kebbab, Z.; Chiker, F.; Sahraoui, K.; Khadraoui, M.; Benramdane, N. Determination of layer thickness and optical constants of thin films by using a modified pattern search method. *Opt. Lett.* **2012**, *37*, 449–451. [CrossRef] [PubMed]

43. Miloua, R.; Kebbab, Z.; Chiker, F.; Khadraoui, M.; Sahraoui, K.; Bouzidi, A.; Medles, M.; Mathieu, C.; Benramdane, N. Peak, multi-peak and broadband absorption in graphene-based one-dimensional photonic crystal. *Opt. Commun.* **2014**, *330*, 135–139. [[CrossRef](#)]
44. Boukabrine, F.; Chiker, F.; Miloua, R.; Kebbab, Z.; Khenata, R.; Prakash, D.; Bin Omran, S.; Verma, K. Combined theoretical studies of the optical characteristics of II-IV-V2 semiconductor thin films. *Opt. Mater.* **2016**, *54*, 200–206. [[CrossRef](#)]
45. Lafort, A.; Kebaili, H.; Goumri-Said, S.; Deparis, O.; Cloots, R.; De Coninck, J.; Voué, M.; Mirabella, F.; Maseri, F.; Lucas, S. Optical properties of thermochromic VO₂ thin films on stainless steel: Experimental and theoretical studies. *Thin Solid Film.* **2011**, *519*, 3283–3287. [[CrossRef](#)]
46. Azam, S.; Khan, S.A.; Minar, J.; Goumri-Said, S. Exploring the electronic structure and optical properties of new inorganic luminescent materials Ba(Si,Al)₅(O,N)₈ compounds for light-emitting diodes devices. *Curr. Appl. Phys.* **2015**, *15*, 1160–1167. [[CrossRef](#)]
47. Liu, M.-L.; Chen, I.-W.; Huang, F.-Q.; Chen, L.-D. Improved Thermoelectric Properties of Cu-Doped Quaternary Chalcogenides of Cu₂CdSnSe₄. *Adv. Mater.* **2009**, *21*, 3808–3812. [[CrossRef](#)]
48. Fan, F.-J.; Yu, B.; Wang, Y.-X.; Zhu, Y.-L.; Liu, X.-J.; Yu, S.-H.; Ren, Z. Colloidal synthesis of Cu₂CdSnSe₄ nanocrystals and hot-pressing to enhance the thermoelectric figure-of-merit. *J. Am. Chem. Soc.* **2011**, *133*, 15910–15913. [[CrossRef](#)]
49. Pei, Y.; Shi, X.; LaLonde, A.; Wang, H.; Chen, L.; Snyder, G.J. Convergence of electronic bands for high performance bulk thermoelectrics. *Nature* **2011**, *473*, 66. [[CrossRef](#)] [[PubMed](#)]
50. Goumri-Said, S. Probing Optoelectronic and Thermoelectric Properties of Lead-Free Perovskite SnTiO₃: HSE06 and Boltzmann Transport Calculations. *Crystals* **2022**, *12*, 1317. [[CrossRef](#)]
51. Goumri-Said, S.; Alrebdi, T.A.; Deligoz, E.; Ozisik, H.; Kanoun, M.B. Revisiting the Electronic Structures and Phonon Properties of Thermoelectric Antimonide-Tellurides: Spin–Orbit Coupling Induced Gap Opening in ZrSbTe and HfSbTe. *Crystals* **2021**, *11*, 917. [[CrossRef](#)]
52. Ding, G.; Gao, G.; Yao, K. High-efficient thermoelectric materials: The case of orthorhombic IV–VI compounds. *Sci. Rep.* **2015**, *5*, 9567. [[CrossRef](#)]
53. Khan, W.; Azam, S.; Kanoun, M.B.; Goumri-Said, S. Optoelectronic structure and related transport properties of BiCuSeO-based oxychalcogenides: First principle calculations. *Solid State Sci.* **2016**, *58*, 86–93. [[CrossRef](#)]
54. Azam, S.; Goumri-Said, S.; Khan, S.A.; Kanoun, M.B. Electronic, optical and thermoelectric properties of new metal-rich homologous selenides with palladium–indium: Density functional theory and Boltzmann transport model. *J. Phys. Chem. Solids* **2020**, *138*, 109229. [[CrossRef](#)]