On the optical characteristics of Cd-Doped gadolinium oxide: A DFT based theoretical study

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This research investigated the optical characteristics of Cd-doped gadolinium oxide Gd_2O_3 by employing density functional theory (DFT) along with the CASTEP simulation package. After the creation of a Gd_2O_3 supercell at an initial $[2 \times 1 \times 1]$ scale, the study evaluated the altered properties of Gd_2O_3 at the supercell level to assess the impact of Cd-doping on the optical features of doped one. Optical properties which were explored included the examining the optical characteristics including the complex dielectric-function, index of refraction, electrical-conductivity, and loss-function. The dielectric function exhibited distinct peaks at certain photon energies that corresponded to various electronic transitions between energy levels of the material. The prominent absorption peaks observed in the energy range of 0.174-1.55 eV for the dielectric-function (imaginary part). This was attributed transitions occurring amongst specific orbitals for pure and Cd-doped gadolinium oxide. The refractive index exhibited stability at lower energy levels, while the conductivity curves displayed excitonic behavior in response to Cd-doping at the supercellular level. Furthermore, the Cd-doping resulted in an increase in absorption, as indicated by the simulated changes in the loss function.

Keywords: DFT; Gd_2O_3; Cd-doping; optical properties; loss function.

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1. Introduction

Gadolinium oxide (also known as gadolinia) is chemical substance having the formula Gd_2O_3. It comes in the form of a white, odourless powder that is acid soluble. This material is available in both bulk and nanoparticle form [1]. Gadolinium is ferromagnetic below Curie point of 21°C (68°F), and has a stronger magnetic field attraction than nickel. Above this temperature, it is element that is best paramagnetic [2]. Due to their distinctive structural and electrical characteristics, which are the result of their 4f electrons, rare-earth sesquioxides find significant uses in the microelectronic, optoelectronic, and optical device industries [3,4]. In several technical fields, including electronics, magnetics, optics, biomedicine, and catalytic converters, lanthanide elements and their compounds play a crucial role. Due to their unusual magnetic properties, gadolinium oxide (Gd_2O_3) nanoparticles are of special interest among these materials. The ability to create unique nanostructures is demonstrated by the fact that Gd_2O_3 nanoparticles may exist in a variety of morphologies, including hollow spheres, nanotubes, nanoplates, nanorods and microrods. These particles have improved chemical and thermal stability in addition to being simple to dope with additional lanthanide ions [5]. Under ambient conditions, 3 A, B, and C polymorphism types of rare-earth sesquioxides occur. The A phase of P3m1 space-group is of hexagonal in nature while the phase B of "C2/m" space-group is monoclinic, and C phase of the Ia-3 space group has a cubic structure. Most sesquioxides with medium-sized cations have cubic or monoclinic crystal structures under ordinary circumstances. Gd_2O_3 was generally observed in cubic form [6]. The unique optical characteristics of gadolinium oxide make it valuable material for broad diversity of optical and optoelectronic applications. Its higher refractive index, potent UV absorption, and high transmittance in visible and near-infrared areas of spectrum make it a desirable material for antireflective coatings, optical fibers, UV-blocking applications, and optoelectronic devices [7]. The electronic properties of gadolinium oxide are particularly essential due to its unique magnetic and optical characteristics. Gadolinium is a rare earth element with seven unpaired electrons, which makes it highly magnetic. When gadolinium oxide is doped with other elements, such as cadmium or terbium, it can emit bright and long-lasting fluorescent light, making it useful in display technologies like LEDs. The electronic properties of gadolinium oxide make it a valuable material for various technological applications, especially those that require high magnetic, optical, or thermal performance [8]. We have selected Gd_2O_3 for our research because it contains many impurities at the atomic level. Currently, there are significant

academic research activities focused on controlling the impurities in Gd_2O_3 to enhance its current physical properties and enable it to behave in new ways. The goal is to regulate the doping of Gd_2O_3 to improve its properties and explore new possibilities for its applications. This chapter focused on studying the properties of pure and cadmium doped gadolinium oxide [8]. The GGA approximation technique is utilized to determine its structural, electronic, and optical characteristics. The analysis of the electronic density of states (DOS) is a powerful technique for studying optical characteristics of a compound. This method can effectively investigate the optical characteristics of a compound in reality. In theoretical calculations, the LDA and empirical-pseudo potential approach are commonly utilized. However, it had been demonstrated that GGA is much greater effective in calculating bandgaps compared to LDA. GGA method is utilized in the current theoretical analysis to calculate the optical properties and bandgaps of gadolinium oxide. In this study, the aim is to investigate the complex dielectric-function, index of refraction, electrical-conductivity, and loss-function of Gd_2O_3. The impact of cadmium doping on the characteristics of gadolinium oxide can depend on concentration and distribution of the dopant atoms, as well as the specific properties being studied and the influenced on the optical properties when Cd-doping have performed on the structure of Gd_2O_3 at supper cellular level. The calculations is done while using the density-approximation i.e. local and generalized with computational details given in subsequent section.

2. Computational details

All computations in this study were performed utilizing the CASTEP code in the Materials Studio (MS) 6.1 software. The software is based on the Density Functional Theory (DFT) approach. DFT is employed to compute the optical characteristics of materials. For general energy, the ultra soft pseudopotential technique is utilized. Ion potential is substituted with ultra-soft pseudopotential when using plane wave basis groups, which unfold the electronic wave function. Ions and electrons are included in the technology for ultra-soft pseudopotentials. The cut-off plane-wave energy is chosen at 571 eV for total-energy and spectra computations. The exchange correlation potential is determined using two different approximations: the generalized gradient approximation (GGA) within the Perdew Burke Ernzerhof (PBE) function and the local density approximation (LDA) [9-11]. The Ultrasoft pseudopotential method is used for ion and electron interactions in this study, and the total energy convergence achieved is 1×10^{-5} YeV/atom. The limited memory Broyden Fletcher Goldfarb Shanno (LBFGS) approach is a dependable technique for conducting a complete relaxation of lattice variables and interior coordinates to optimize the structure. The convergence parameters for maximum stress and displacement were imposed at 0.05 GPa and 0.001Å, respectively. Figure 1 depicts a cubic phase unit cell of Gd_2O_3 with four Gd atoms and 18 O atoms, 2 non-equivalent Gd one

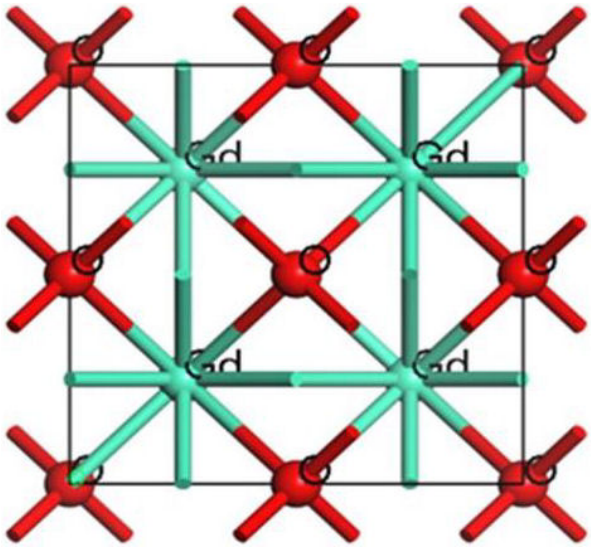

FIGURE 1. Cubic structure of Gd_2O_3. The large and tiny spheres represent the atoms Gd and O, respectively.

at sites 24b and 8b. In addition to this, 1 O atom is present at site 48e. The optical characteristics of pure gadolinium oxide and Cd-doped Gd_2O_3 were analyzed using a primitive cell. The Monkhorst Park technique was applied to integrate the Brillouin zone, using a k-point mesh of $3 \times 3 \times 3$ and a cut-off energy of 571 eV.

In the current study, we have considered the configurations of Gd_2O_3 as Gd where $4f^7 5d^1 6s^2$ representing the valence states of Gd atoms and $2s^2p^4$ as valence states of O atoms. As we proceed, we create a Gd_2O_3 supercell with a scaling of (211) and examined the optical characteristics such as Dielectric function, Refractive Index, optical Conductivity and Loss function by using DFT. Subsequent to this, one Gd atom out of eight is replaced with Cd atom at supper cellular level and recalculate the aforementioned properties.

3. Results and discussion

The unit cell of Gd_2O_3 was replicated to create a supercell with a $2 \times 1 \times 1$ configuration, which contains 39 atoms with 8 Gd and 31 O atoms. A gadolinium atom was replaced by a cadmium atom in the crystal, known as cadmium doping, as shown in Fig. 2. Our goal is to examine the structural alteration and enhanced characteristics of Gd_2O_3 while doping Cd at the supercell level. We now have the modified complex dielectric function, index of refraction, electrical conductivity, and loss function calculations for this unit cell. When an atom of gadolinium in a Gd_2O_3 crystal is replaced by an atom of cadmium, it is called cadmium doping. The impact of cadmium doping on the features of gadolinium oxide depends on the concentration and distribution of the dopant atoms, as well as the specific properties being studied. For Cd-doped Gd_2O_3 structure with space group Pn-3m, lattice parameters are $a = 10.715$Å, $b = c = 5.358$Å, and cell angles are $\alpha = \beta = \gamma = 90^\circ$. Fine-quality pseudopotentials with an

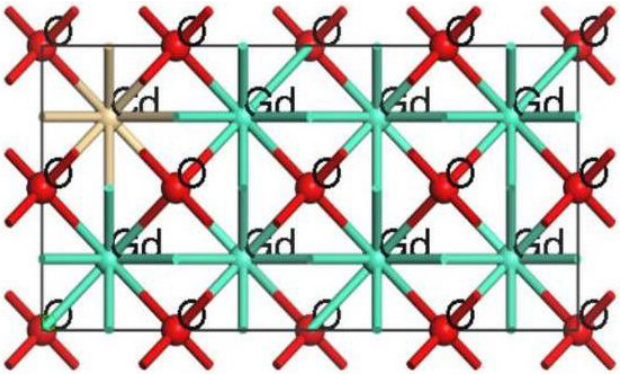

FIGURE 2. Crystal structure of $2 \times 1 \times 1$ supercell of Cd-doped Gd_2O_3.

energy cut-off of 250 electron volts (eV) were utilized to emulate the interaction between the valence electrons and conduction holes precisely for Cd-doped gadolinium oxide. By using an energy cut-off of 250 eV, the calculations of optical features were able to produce accurate and optimized results. To perform k-point grid sampling of the reduced Brillouin zone using the Monkhorst Pack scheme, a $3 \times 3 \times 3$ grid was set for pure Gd_2O_3 while a $1 \times 1 \times 1$ grid was used for Cd-doped Gd_2O_3. During the geometry optimization, the energy convergence for this Cd-doped structure is 1.209×10^{-6} eV/atom, the highest displacement is 0.001Å, the highest stress is 0.03 GPa, and the highest force is 0.03 eV/Å. The total volume of lattice parameters is 307.589Å^3. When Cd is introduced as a dopant in a material, the lattice parameters a, b, c, and the unit cell volume V observed to increase. Additionally, the band gap Eg of the material is found to decrease with the incorporation of Cd dopants [12].

The impact of cadmium doping on the optical characteristics of gadolinium oxide can be studied, which reveals that the introduction of a dopant atom can have a number of effects on the properties of a material, including optical as well as other properties. When a single atom of gadolinium in a Gd_2O_3 crystal is replaced by an atom of cadmium, the optical features of the material are affected, and adding dopants can also create defects or distortions in the crystal lattice, which affects the mechanical, thermal, or chemical stability of the material. Additionally, dopants can interact with other defects or impurities in the material, leading to further changes in its properties [13].

3.1. Effect of Cd Doping on the Optical Characteristics of Gd_2O_3

The significance of optical properties is often emphasized through various parameters, such as absorption coefficient, reflectivity, refractive index, dielectric function, and loss function. All the above-mentioned are interconnected with the complex dielectric function equation, and the dielectric function, denoted as $\epsilon(\omega)$, can be expressed as:

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega).$$

The real part of the dielectric function $\epsilon_1(\omega)$ is due to the level of electronic polarization, and the Kramers-Kronig relation is used to obtain this real part. The imaginary part $\epsilon_2(\omega)$ is related to dielectric losses of the material. Further to it, other optical characteristics, *e.g.*, absorption coefficient, reflectivity, refractive index, and loss function, can be calculated from $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ by utilizing the Kramers-Kronig relation [14].

The imaginary part of the dielectric function, $\epsilon_2(\omega)$, can be expressed as:

$$\epsilon_2(\omega) \propto \frac{1}{\omega^2} \sum_{n,m} \int_{BZ} dk \, |P_{nm}|^2 \, \delta(\epsilon_m(k) - \epsilon_n(k) - \omega).$$

The imaginary part of the dielectric function $\epsilon_2(\omega)$ is associated with the combined density of states (DOS) and momentum matrix elements. The Kramers-Kronig relation can be employed to derive the real part of the dielectric function, $\epsilon_1(\omega)$ [15].

The electron energy-loss function is defined as:

$$L(\omega) = \frac{\epsilon_2(\omega)}{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)}.$$

The $L(\omega)$ parameter is a useful method for examining different properties of the material, as it characterizes energy-loss of electrons with high-speed enacting across the doped-material. The prominent peak's presence in this function is attributed to plasma oscillations. Figure 3 displays the computed real and imaginary parts of the dielectric function for pure and Cd-doped Gd_2O_3 crystal structure utilizing the GGA+U methods, up to an energy magnitude of 28 eV. The significant range of variation in the dielectric function suggests that Gd_2O_3 has the potential for use in high-frequency UV device applications. The dielectric function exhibits distinct peaks at certain photon energies. These peaks correspond to electronic transitions between different energy levels in the material. The prominent absorption peak observed in the energy range of 0.174-1.55 eV for the imaginary part of the dielectric function is a result of energy transitions occurring between specific orbitals for pure and Cd-doped Gd_2O_3. For pure Gd_2O_3 adjacent to the primary peaks, there are smaller peaks present at 10.2 eV, which arise from govern transitions among the corresponding orbitals, *i.e.*, Gd-5d and O-2s. Similarly, subsequent peaks at 12.7 eV also correspond to direct transitions among relevant orbitals, *i.e.*, O-2s to Gd-5d. Compared to pure gadolinium oxide, the dielectric function of Cd-doped gadolinium oxide can show differences in peak positions and alterations to its overall shape [16]. The real and imaginary components of the dielectric function can be utilized to compute several other crucial optical functions, such as the refractive index $n(\omega)$ and the extinction coefficient $k(\omega)$. By utilizing the dielectric function, which explains the material's regards to an applied electric field, these optical functions can be determined and provide valuable information about the material's behavior in various optical applications [17].

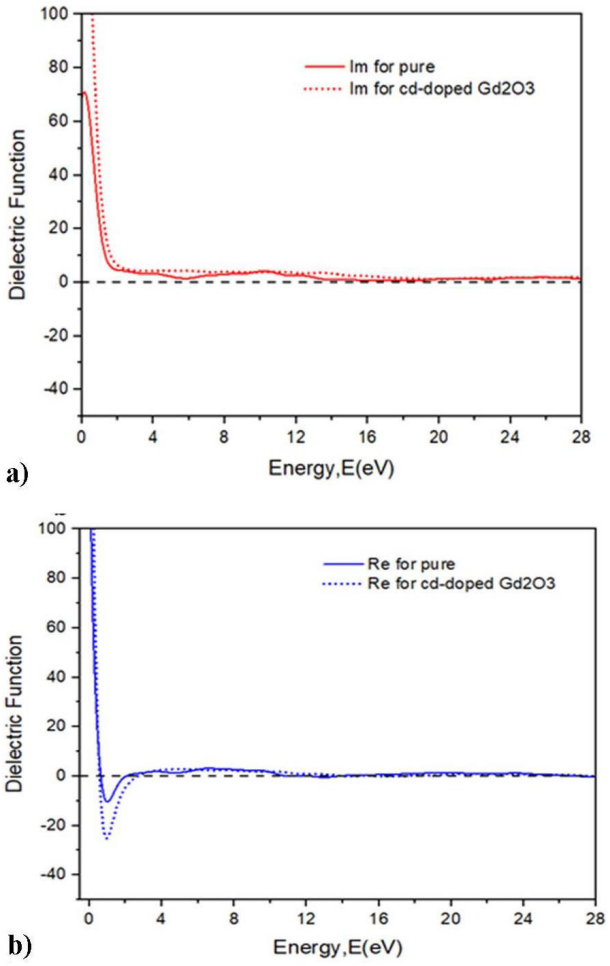

FIGURE 3. Dielectric Function for pure and Cd-doped Gd_2O_3 crystal structure.

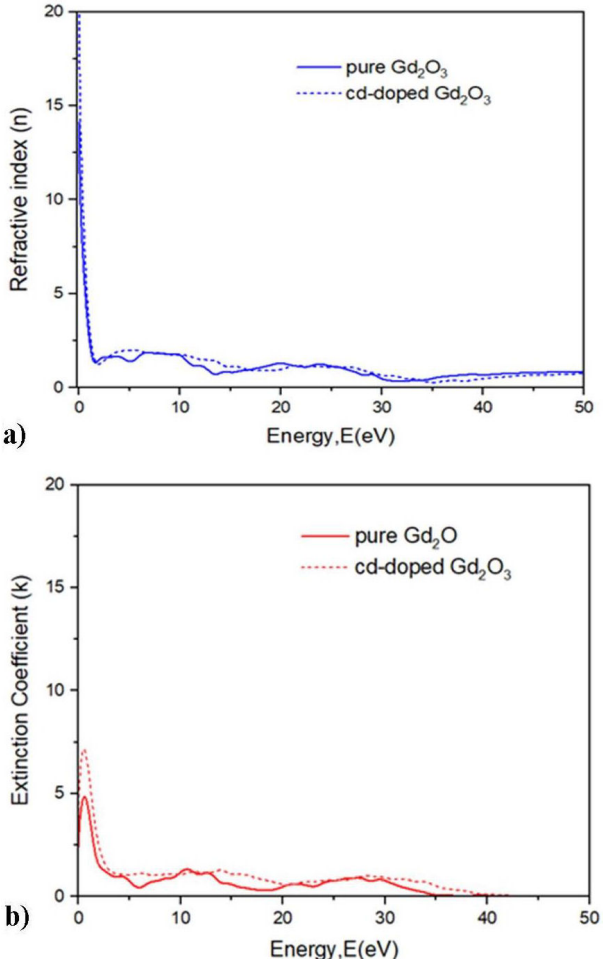

FIGURE 4. Refractive index n and extinction coefficient k for pure and Cd-doped Gd_2O_3 crystal structure.

Figure 4a), 4b) illustrates the results of the refractive index n and extinction coefficient k for pure and Cd-doped Gd_2O_3 crystal structure. The refractive index remains relatively stable at lower energy levels, but as energy levels increase, it reaches a maximum value and then begins to decrease. Using the GGA methods, the constant refractive index $n(0)$ was noticed to be from point 11 to 1.34, respectively. In the visible region, the refractive index increases with energy and peaks at 0.075 eV in the ultraviolet region. While the refractive index is strongly linked to bonding, any process that boosts the electron density among the material will also increase the refractive index. The refractive index decreases with increased energy for both undoped and doped gadolinium oxide. The refractive index is a determinant of how much the speed of light is decreased when it passes through a material [9].

The optical conductivity is a measure of how much current can flow in a material when it is exposed to light. By using DFT, one can predict the optical conductivity of gadolinium oxide, which is an important parameter for designing optoelectronic devices.

Figure 5 illustrates the computation of the optical conductivity for pure and Cd-doped Gd_2O_3 crystal structure as a function of energy. Exciton is formed when an electron and electron-hole are bound together and move through the periodic structure of a crystal. The optical conductivity plot reveals the presence of excitonic behavior within the energy ranges of 9.79-10.6 and 25.3-26.8 eV. The optical conductivity plot for Cd-doped reveals the presence of excitonic behavior within the energy ranges of 10.79-11.9 and 26.3-29.8 eV. These peaks occur as electrons transition from valence bands of O-2p and O-2s to the conduction band of Gd-5d. The optical conductivity of gadolinium oxide refers to the material's ability to conduct electricity in response to light, and it is a measure of how the material absorbs and reflects light at various energy levels. The analyses of the optical conductivity curve, we can learn about the behavior of electrons in the material and the transitions that occur between energy levels [18].

Figure 6 shows the electron energy loss spectrum of Gd_2O_3 in its cubic phase, which refers to the material's ability to absorb energy and the corresponding electrons losing energy within the material. The peaks within the spectrum are a result of various processes, including interband and in-

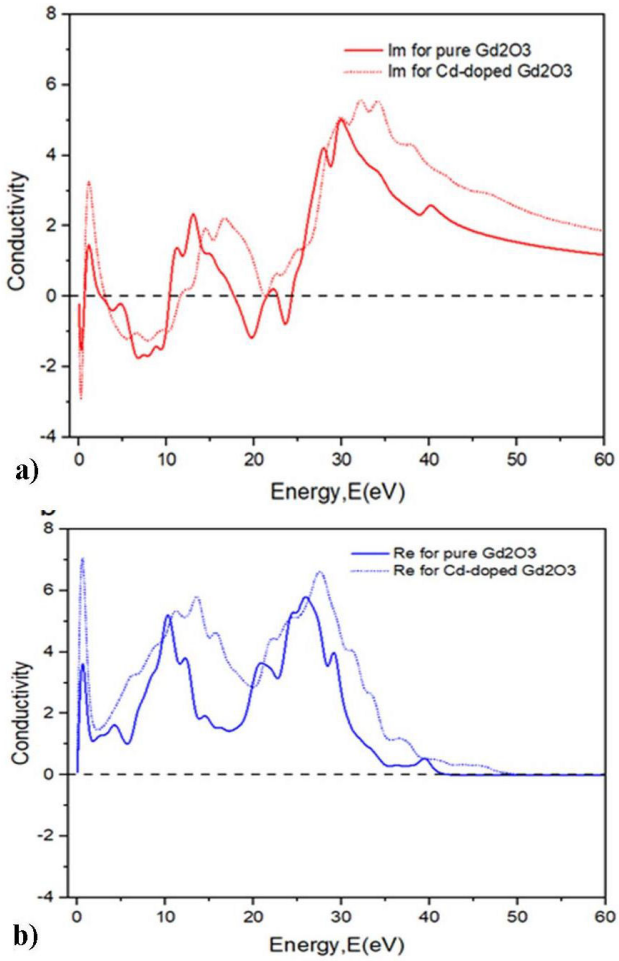

FIGURE 5. Optical conductivity spectrum for pure and Cd-doped Gd_2O_3 crystal structure.

traband excitations, as well as the excitation of charge carrier Plasmons. These peaks provide important observations into the electronic structure and bonding of the material.

The initial peak found at 4.92 eV can be traced back to the transition of electrons from O-2p to Gd-5d orbital. Additionally, the real component of the dielectric function at the point ($\epsilon_1(\omega) = 0$) might indicate the presence of a plasma resonance. Upon examining the $\epsilon_1(\omega)$ spectrum, a zero value of $\epsilon_1(\omega)$ can be observed at 31.5 eV, which relates to the Plasmon peak found within the $L(\omega)$ spectrum.The highest energy peak in the $L(\omega)$ spectrum is 32.15 eV, which corresponds to the volume energy of Plasmon, *i.e.*, $h\omega_p$. This energy arises from the excitation of electrons from the O-2s orbital to the upper and lower conduction bands. For Cd-doped gadolinium oxide crystal structure, the initial peak found at 19.2 eV can be traced back to the transition of electrons from O-2p to Gd-5d orbitals. Additionally, the real component of the dielectric function at the point ($\epsilon_1(\omega) = 0$) might indicate the presence of a plasma resonance. Upon examining the $\epsilon_1(\omega)$ spectrum, we can observe that the value of $\epsilon_1(\omega)$ is zero at 39.5 eV, which relates to the Plasmon peak found within the $L(\omega)$ spectrum. The highest energy peak in the $L(\omega)$ spectrum at 39.5 eV corresponds to the volume Plasmon energy, $h\omega_p$. This energy may arise from the excitation of electrons from the O-2s orbital to both the Upper and lower conduction bands.

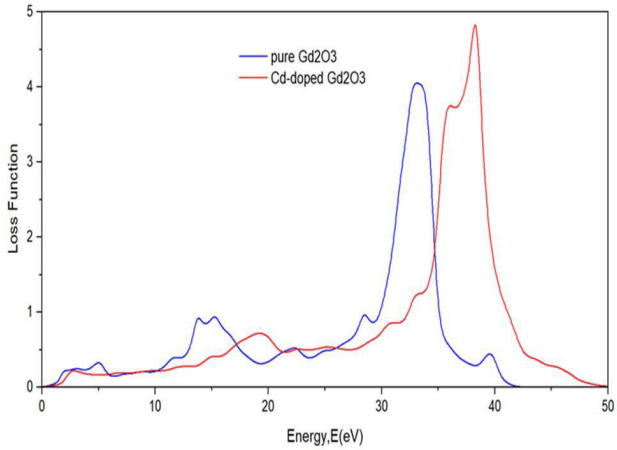

FIGURE 6. Loss function for pure and Cd-doped Gd_2O_3 crystal structure.

4. Conclusion

In this study, optical characteristics of cubic pure and Cd-doped Gd_2O_3 within a density functional theory framework were investigated. This computational investigation extensively examined the optical properties of pure and Cd-doped Gd_2O_3 at the super-cellular level. After optimizing both structures, the analysis focused on the optical properties, revealing significant insights into the dielectric function, refractive index, conductivity, and loss function, which are:

- The analysis of dielectric function for pure and doped gadolinium oxide showed that the significant absorption peak detected in the imaginary part of the dielectric function, ranging from 0.174 to 1.55 eV, can be attributed to energy transitions occurring between specific orbitals within pure and Cd-doped gadolinium oxide.

- The refractive index exhibited a relatively stable behavior at lower energy levels, but as energy levels increased, it reached a maximum value and then started to decrease. By utilizing GGA methods, the static refractive index $n(0)$ was determined to range from 1.11 to 1.34 for undoped and doped gadolinium oxide, respectively.

- The conductivity curves exhibited excitonic behavior with peaks resulting from electron transitions, and the loss function of gadolinium oxide represented the material's capacity to absorb energy and the associated energy loss of electrons within the material. The peaks observed in the spectrum were attributed to diverse processes, including interband and intraband excitations.

Based on our analysis of Gd_2O_3, it was determined that the material demonstrated a high degree of optical transparency in the UV region and possessed a high refractive index. These characteristics make Gd_2O_3 well suited for applications in UV optical devices.

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