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Study of the Structural, Electronic and Optical Properties of $GdV_{(1-y)}M_yO_4$ (M = P / (y = 0.25 , 0.75))

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Abstract

This study presents a sophisticated simulation-driven analysis employing first-principles density functional theory (DFT) calculations to investigate the electronic properties, optical and structural of $GdVO_4$ doped with phosphorus (P). $GdVO_4$ is a member of the rare-earth orthovanadate ($REVO_4$) family, which encompasses rare-earth elements such as the lanthanides (La to Lu), yttrium (Y), and scandium (Sc). The study examines the impact of phosphorus doping at concentrations of 25% and 75% on key properties, including the crystal structure, band structures, and optical characteristics such as the absorption coefficient. Advanced DFT-based computational tools, as implemented in the CASTEP software package, were utilized to perform the analysis. The results underscore the potential for unveiling novel properties of phosphorus-doped $GdVO_4$, offering valuable insights and opening new avenues for future research in this domain.

Keywords:

P-doped GdVO4, Ab-initio methods, CASTEP code, Structural properties, Optical properties, Electronic properties, Density functional theory calculations, Rare-earth elements.

Introduction

Orthovanadates have various applications, including being used as laser materials with rare earth**.** Doping orthovanadates with them is particularly beneficial for laser applications. These elements can introduce energy levels within the material that light can excite, leading to efficient laser emission. Rare earth vanadates, denoted as RVO_4 (where R = La, Ce, Nd, Sm, Eu, Gd) **[1]**. They exhibit interesting optical, and electrical properties. Optical characteristics are one of the most prominent features aimed at their applications in optical devices such as polarizers and laser hosts **[2];** for example, Among the vanadate laser hosts, gadolinium vanadate ($GdVO_4$) Crystal has recently attracted much attention as an essential laser host material due to its excellent thermal and optical properties **[3]**. It exhibits high absorption and emission cross-sections of the RE ions doped in this gain medium and high thermal conductivity two times higher comparable to YAG **[4–5]**. For these reasons and others, as our research topic, we chose to study $GdVO_4$ and the effect of doping it with one of the famous elements on its properties.

Phpsphore is the most important of elements, and GdVO4 should preferably be doped with it. P: $GdVO_4$, which is the subject of our research, is a widely used laser material known for its efficient emission properties achieved by doping with Phpsphore . This way has been proven by some studies, such as those conducted by Yang et al **[6]**. These excellent properties lead us to predict high laser performance.

Similar to other rare earth vanadate compounds, $GdVO_4$ crystallizes with a unique tetragonal zircon-type space group (I41/amd) structure, accommodating four molecules per unit cell **[9].** The process of Phpsphore doping in P: $GdVO_4$ is equally intriguing. Phpsphore ions replace the V^{5+} sites in the crystal lattice, Herein, we briefly describe one of the methods for synthesizing P: $GdVO_4$.

First, Gadolinium phosphovanadate is synthesized using the solution combustion method. High-purity starting materials, including gadolinium nitrate hexahydrate ($Gd(NO_3)_3{\cdot}6H_2O$), ammonium metavanadate (NH_4VO_3), ammonium phosphate ($NH_4H_2PO_4$), urea (CH_4N_2O), and samarium and thulium nitrates ($Sm(NO_3)_3{\cdot}6H_2O$), are used. The materials are dissolved in deionized water in appropriate proportions to form a precursor solution. The solution is mixed thoroughly using a magnetic stirrer at around 70°C for 30 minutes, resulting in a homogeneous yellowish solution. The solution is then transferred to ceramic crucibles, which are placed in a preheated furnace at 600 ± 10°C.

During the process, exothermic reactions produce light fluffy ash as the final product. The ash is cooled to room temperature in air and manually ground using a mortar and pestle to obtain a fine powder. Finally, the powder undergoes annealing at 900°C for 2 hours in air to enhance its crystalline structure.

[10].

In this paper, we investigated the properties of $GdVO_4$ before and after phosphorus doping. Doping levels of 25% and 75% were employed, resulting in the compounds $GdV_{0.75}P_{0.25}O_4$ and $GdV_{0.25}P_{0.75}O_4$, respectively. We then compared the properties of the undoped and doped materials to assess the impact of doping on the crystal characteristics. To the best of our knowledge, limited studies have compared theoretical calculations of structural, electronic, and optical properties with experimental results **[10]**, especially those focusing on varying doping ratios. This aspect constituted the primary focus of our research. In the following sections, we outline the computational details and methodology adopted in this study. We then calculate the physical properties of zircon-structured $GdVO_4$ doped with phosphorus at doping levels of 25% and 75%. The simulation results are presented and the key findings thoroughly discussed.

Finally, we conclude by emphasizing the most significant outcomes of this research.

2.Results and discussion

2.1 Structural Properties

a) Lattice parameters

We adjusted the lattice parameters before calculating the electronic and optical properties. **Figure 1** shows the crystal structure of zircon-type $GdVO_4$ in space group I41/amd. For zircon structure $GdVO_4$, the Gd atoms are located at the Wyckoff position 4a (0, 0.750, 0.125), the V atoms are at 4b (0, 0.250, 0.375), and the O atoms are at 16 h (0, 0.432, 0.203**) [11].**

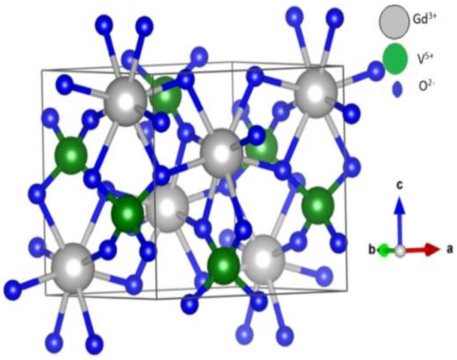

Figure 1. Crystal structure of $GdVO_4$ (space group: I41/amd)

The optimized lattice parameters for $GdVO_4$, $GdV_{0.75}P_{0.25}O_4$ and $GdV_{0.25}P_{0.75}O_4$ are listed in **Table 1.**

The compounds	The Lattice parameters	Methode
		GGA-PBE
$GdV_{0.75}P_{0.25}O_4$	a,b(Å)	7,285
	c(Å)	6,425
	V(Å^3)	341,68045
$GdVO_4$	a,b(Å)	7,39
	c(Å)	6,53
	V(Å^3)	356,617013
$GdV_{0.25}P_{0.75}O_4$	a,b(Å)	7,075
	c(Å)	6,215
	V(Å^3)	311,807324

Table1. The lattice parameters for $GdVO_4$, $GdV_{0.75}P_{0.25}O_4$ and $GdV_{0.25}P_{0.75}O_4$ calculated with GGA-PBE.

Numerous studies have demonstrated that the experimental values of the unit cell parameters for the $GdVO_4$ compound, specifically the dimensions *a (b)*, *c*, and the volume *V*, fall within the approximate values of 7.2122 Å, 6.3460 Å, and 330.1000 Å^3, respectively (Donald F. Mullica et al) **[12]**. As shown in **Table1**, the deviations between the theoretical and experimental values of the lattice parameters (*a*, *b*, and *c*) do not exceed 3.00%. Consequently, the results obtained from our calculations are in excellent agreement with the experimental data and other findings reported by Donald F. Mullica et al.

Upon analyzing the volume parameter (*V*), a significant decrease is observed following the doping process. This reduction is expected, as phosphorus atoms are smaller than vanadium atoms **[13]**. Consequently, as the doping ratio of phosphorus atoms increases, the volume decreases gradually. These results are in close agreement with the previously presented interpretation and confirm the simulation results, and the tabulated data reinforce this observation.

b) bulk modulus B_0

Experimental results **[11]** agree with the GGA-PBE calculated results (114.08 GPa). Observations from the **Table 2** values indicate that the bulk modulus increases with increasing phosphorus doping concentration, which is in excellent agreement with theoretical predictions. When doping $GdVO_4$ with phosphorus, where vanadium (V) atoms are replaced by phosphorus (P) atoms at proportions of 25% and 75%, the bulk modulus increases due to changes in the crystalline structure and chemical properties of the material. Phosphorus has a slightly smaller ionic radius compared to vanadium and tends to form stronger and more stable bonds with oxygen, as observed in P–O bonds within phosphate groups (PO_4^{3-}). These bonds are more robust and shorter than V–O bonds, which enhances the rigidity of the crystal lattice and reduces its compressibility, thereby increasing the bulk modulus. The incorporation of phosphorus reduces the presence of crystallographic defects in the original material, improving the structural uniformity and enhancing its resistance to compression. Moreover, the electronic configuration of phosphorus contributes to strengthening the bonding within the crystal lattice, making the material more resistant to volumetric changes under pressure. When the doping proportion is increased to 75%, the chemical bonds become even more stable, resulting in a significant rise in the bulk modulus compared to the 25% doping level.

The increase in bulk modulus resulting from doping brings several optical benefits. For instance, the enhanced material density raises the refractive index, making the material more efficient at focusing or bending light, which is advantageous for optical applications such as lenses and laser components. Additionally, the improvement in the crystal lattice reduces internal light scattering, thereby enhancing the material's transparency at specific wavelengths.

.The compounds	**bulk modulus B_0 (GPa) (GGA-PBE)**
$GdV_{0.75}P_{0.25}O_4$	130,7116925
$GdVO_4$	114.08
$GdV_{0.25}P_{0.75}O_4$	163,9673775

Table 2. The bulk modulus for $GdVO_4$, $GdV_{0.75}P_{0.25}O_4$, and $GdV_{0.25}P_{0.75}O_4$ calculated with GGA-PBE **.**

2. Electronic band structure

In this study, our main objective is to gain a deeper understanding of the electronic band structure and how it affects the optical properties of P-doped $GdVO_4$. To achieve this, we employed several ab initio methods from the density functional theory (DFT) implemented in the CASTEP (Cambridge Serial Total Energy Package) code.

To investigate the influence of electronic band structure on the optical properties of certain compounds, we conducted first-principles calculations using the DFT approach (GGA-PBE). **Figure 2** illustrates the electronic band structure of both pure $GdVO_4$ and $GdVO_4$ doped with P atoms.

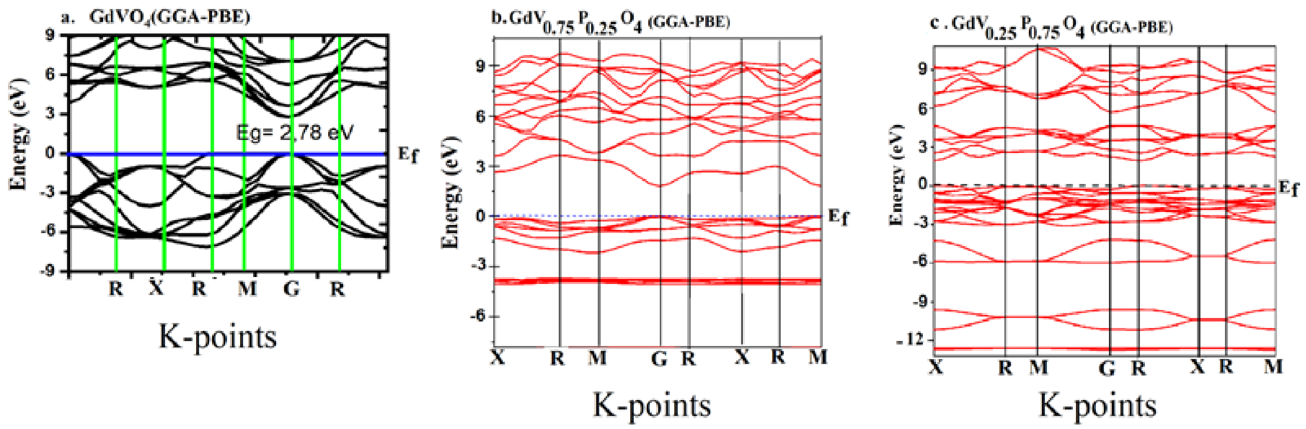

Figure 2. Electronic band structure for (a) $GdVO_4$, (b) $GdV_{0.75}P_{0.25}O_4$ and (c) $GdV_{0.25}P_{0.75}O_4$.

The figure investigates the significant impact of doping on the bandgap of the pristine $GdVO_4$ compound. As illustrated in **Figure 2a**, the undoped material exhibits a bandgap of approximately 2.78 eV. Upon introducing 25% phosphorus (P) to form $GdV_{0.75}P_{0.25}O_4$, a slight modification in the band structure is observed. The bandgap narrows relatively compared to the pristine structure, as shown in **Figure 2b**. This change reflects an increase in the density of electronic states near the Fermi level (E_f), leading to a decrease in the gap energy to about 1.8 eV.

When considering **Figure 2c**, with an increased phosphorus content of 75% in the $GdV_{0.25}P_{0.75}O_4$ compound, the electronic structure becomes closer to that of $GdPO_4$, which possesses an indirect bandgap. Estimates of the bandgap in this compound indicate values ranging from 3.5 to 4.0 eV, exhibiting indirect bandgap characteristics. In this type of gap, the highest point in the valence band does not align with the lowest point in the conduction band along the k-points axis. This type of gap reduces the efficiency of light emission, as electron transitions between the bands require phonon assistance, making it less suitable for laser applications compared to direct bandgaps. Conversely, if the bandgap is direct, as in the $GdV_{0.75}P_{0.25}O_4$ compound, light emission is more efficient, opening the possibility for its use in laser applications with higher efficiency.

In summary, doping $GdVO_4$ with varying concentrations of phosphorus leads to significant changes in the bandgap, transforming the material's properties to make it adaptable to various optical applications, especially in the field of lasers that require specific wavelengths.

3. The absorption coefficient

The analysis and interpretation of the absorption coefficient indicate that the spectrum in **Figure 3.a** for the base compound $GdVO_4$ spans an energy range of 0 to 50 eV, displaying prominent absorption peaks around 20 eV and 30 eV. These peaks suggest active electronic transitions at these energy levels, likely associated with electron transitions involving vanadium and oxygen atoms. In **Figure 3.b**, for the compound $GdV_{0.75}P_{0.25}O_4$ with 25% phosphorus doping, a general decrease in the absorption coefficient is noted compared to the base compound. The absorption becomes concentrated in a lower energy range (5 eV to 20 eV), and the sharp peaks observed in the base compound diminish. This change reflects the impact of doping on reducing the density of available electronic states for transitions. With an increase in doping concentration to 75% in **Figure 3.c** for the compound $GdV_{0.25}P_{0.75}O_4$, a further reduction in the absorption coefficient is observed compared to the previous two compounds. Absorption becomes confined to a range of 10 eV to 25 eV, with less pronounced peaks. This indicates an enhanced effect of doping in reducing electronic transitions, as phosphorus alters the electronic distribution and reduces the energy levels contributing to the absorption process. The effect of doping and the increase in phosphorus concentration are evident in the observed changes in the material's electronic structures. The introduction of phosphorus partially replaces vanadium, altering energy levels and electronic transition states.

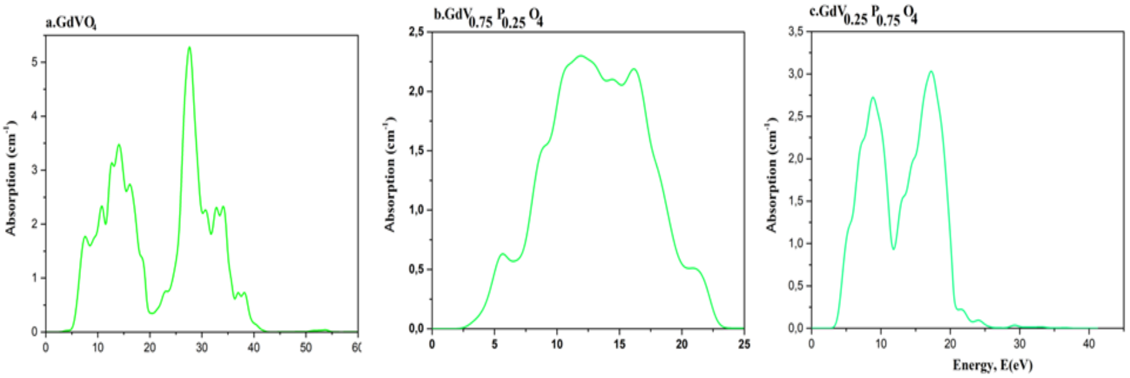

Figure 3. The the absorption coefficients of (a) $GdVO_4$,

(b) $GdV_{0.75}P_{0.25}O_4$, and (c) $GdV_{0.25}P_{0.75}O_4$.

As the doping concentration increases, the density of available electronic states decreases, explaining the reduction in the absorption coefficient. Additionally, phosphorus doping contributes to reducing the sharpness of the peaks and broadening the absorption spectrum, thereby improving the material's properties for optical applications. Furthermore, doping reduces absorption at higher energies, which is particularly beneficial for laser applications requiring materials with high transparency in the higher energy range. In conclusion, phosphorus doping in $GdVO_4$ leads to a reduction in the absorption coefficient and an increase in transparency in the higher energy range. With higher doping concentrations, absorption decreases further, making the materials more efficient as laser-active media. The ability to tune absorption through doping contributes to the development of optical materials that can be effectively used in laser technologies and advanced electronic applications.

4.Conclusion

In this study, we simulated and analyzed the structural, electronic, and optical properties of the $GdVO_4$ compound, focusing on the effects of phosphorus doping. Structurally, the results showed that the introduction of phosphorus leads to significant changes in the unit cell volume, reflecting the impact of doping on the material's crystalline structure. Electronically, it was found that phosphorus doping reduces the energy band gap, contributing to an increase in the density of electronic states near the Fermi level.

Regarding optical properties, the analysis of the absorption coefficient revealed that phosphorus doping reduces the absorption coefficient and increases transparency in higher energy ranges, making the material more efficient for laser applications. Additionally, the study demonstrated that phosphorus doping enhances the material's hardness and reduces its compressibility, as evidenced by the evaluation of the bulk modulus.

The study concludes that phosphorus doping in the $GdVO_4$ compound enhances its structural, electronic, and optical properties, paving the way for the development of advanced optical materials that contribute to innovation in optical and electronic technologies.

In the future, we aim to investigate the effects of doping with other elements to develop new materials with improved properties. Moreover, the current findings represent an important step toward the application of these materials in advanced technologies, such as laser systems and electronic devices.

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