Medbiotech Journal

MBTJ, 5(3): 37-40, 2021

Research Paper

First-principles calculations on photocatalytic activity of ZnWO4 doped with Lithium

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Received: 15 June 2021 Accepted: 05 July 2021 Published: 02 September 2021

Abstract

In this paper, ZnWO4 -doped with of Li. dielectric and the consequent optical refraction constants have been calculated according to density function theory (DFT) and by using CASTEP calculation method. GGA approximation has been used for correlation and exchange effects and results have been compared by experimental results. The calculations showed that doped ZnWO4 with Li (18.8%), dielectric constant will increase and structure of the main spectrum goes toward less energy which satisfies the corresponding experimental data result. The theoretical data reveal that main contributors in the valence band of ZnWO4 are the Zn 3d-, W 5d- and O 2p-like states: the Zn 3d- and W 5d-like states contribute mainly at the bottom, whilst the O 2p-like states at the top of the valence band, with also significant portions of contributions of the above states throughout the whole valence-band region of the tungstate under study. The DFT calculations suggest that the Li doping and the induced OVs can narrow the band gap which enhances photocatalytic activity in the visible light region.

Keywords: photocatalytic activity, Castep, Dielectric constant, Optical properties, Zinc tungstate ($ZnWO_4$)..

How to cite the article:
N. Madadi Mahani, First-principles calculations on photocatalytic activity of ZnWO4 doped with Lithium, Medbiotech J. 2021; 5(3): 37-40. https://dorl.net/dor/20.1001.1.22092528.2021.05.03.7.5

Introduction

The zinc tungstate ($ZnWO_4$) is non-hygroscopic and chemically resistant [1]. Also, ZnWO4 has intrinsic photocatalytic activity. ZnWO4 is introduced by high average refractive index, high light yield, , short decay time, high X-ray absorption coefficient and low afterglow to luminescence and is considered to be a promising material for dosimetry and computed tomography and Xray [2]. $ZnWO_4$ as well as has been used as optical fibres, scintillation materials, heterogeneous catalysts [3] and scintillating bolometers [4].

But the pure ZnWO4, as a monoclinic wolframite tungstate metal oxide with $d^{10}s^2d^0$ electronic configuration, photocatalytic efficiency is not very high because the ZnWO4 has a high electron-hole recombination rate and only absorbs the ultraviolet wavelengths with low visible light absorption utilization rate [5]. However, the actual photocatalytic performance of pristine ZnWO4 is still markedly restricted by its wide band gap Doping is also a method as well as a popular synthesis method for increasing the optical efficiency of ZnWO4, and rare-earth (RE) is an important research object to increase the efficiency of ZnWO4 photocatalysis due to its rich energy level, particular 4f–5d and 4f–4f electronic transition characteristics [6] Li+ as a charge compensation agent can improve the luminescence performance of phosphors [7], so here we studied Li+-doped ZnWO4 materials and investigated its photocatalytic properties.

The effect of Ce3+ doping on the structure, morphology, optical properties and photocatalysis of ZnWO4 has been studied by Phuruangrat et al [8]. La3+-doped ZnWO4 nanorods with an

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abundance of OVs were synthesized by a simple hydrothermal method. The photocatalysts exhibited excellent NO removal activity and strong inhibition of the toxic intermediate (NO2). The DFT calculations of La3+-doped ZnWO4 nanorods has been suggested that the La3+ doping and the induced OVs could narrow the band gap and enhance light utilization [9].

In this study, the effect of increasing of Li to zinc tungstate and the impact of dopant concentration have been investigated by using molecular simulations on optical and dielectric properties of Li-ZnWO4 doped. To investigate these properties, we performed ab-initio pseudopotential calculations with the GGA of the density functional theory (DFT).

Experimental section and procedures

ZnWO4 crystallizes in a monoclinic wolframite-type structure (P2/c space group) with unit cell parameters as follows: a = 4.69263 A, b = 5.72129 A, c = 4.92805 A, β = 90.6321 [10]. Periodic DFT calculations were carried out with electron exchange correlation was treated with generalized gradient approximation (GGA) within Perdew-Wang 91(PW91) functional [11]. Considering the similar ionic radius and charge balance, the Li+ atoms will preferentially occupy the Zn2+ position in the ZnWO4 host, because the ion radius of Li+ (76pm) is close to the ionic radius of Zn2+ (74pm) but larger than that the W6+ (60pm) radius. The super cell 4 × 4 × 2 has been used in this study (figure 1).

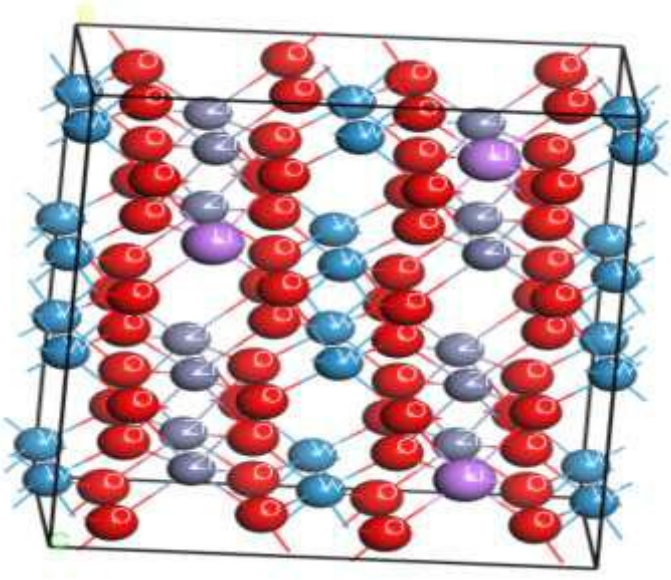

Fig 1: Crystal structure of $ZnWO_4$ doped with 3 Li

Result and discussion

As can be seen the energy gap of doped samples is less than that of a pure form. Increasing the Li will result in the enhancement of the magnetic properties of the sample. As a result, the interactional potential becomes stronger and the energy gap is reduced in relation to pure form. According to the energy gap, we find that at first energy gap decreases by increasing Li.

The linear response of a structure to the electromagnetic radiation can be described using dielectric function. The electronic dielectric function is defined as [12]:

$$\epsilon_{exp}=\epsilon_{inter}(w)+\epsilon_{intra}(w) \quad (1)$$

Where ω, ε1(ω) and ε2(ω) refer to incoming light frequency, real part and imaginary part of dielectric function respectively.

In Figure 2, the real part of the dielectric function and refractive index has been shown for Li-ZnWO4 sample. Waves will not be published in these areas. In these areas, called unauthorized areas, we have the processes of absorption and dissipation. Found that by increasing Li concentration, the main structure of the spectral shifted to the lower energies, i. e., the roots of the real part of the dielectric function occurs at lower energies. in zero energy, which has been calculated here by GGA for different concentrations and have been reported in Table 1.

The relationship between the real and imaginary parts of the dielectric function is shown below [13].

$$R_e(\epsilon(w)) = n^2(w) + K^2(w) \quad (2)$$

$$Im(\epsilon(w)) = 2n(w)K(w) \quad (3)$$

Where n (w) is a real part of the refractive index. The static refractive index of the imaginary part, which is also called extinction coefficient. Extinction coefficient for a substance is measuring the amount of absorption of electromagnetic radiation by that substance. If the electromagnetic wave passes easily through it, the substance has a low extinction coefficient and vice versa, if the radiation penetrates the substance barely, it has a high extinction coefficient. Real part of the refractive index has been shown in Figure 2. The results showed that dielectric constants increases with increasing li. This is the expected result, since the dielectric constant changes are inversely related with the threshold optical transitions, i. e., the trend of gap change.

Table 1: The computational results of static dielectric constant, static refractive index and energy gap for pure and Li-ZnWO4

Sample	static dielectric constant	static refractive index	Energy gap (eV)
ZnWO4	6.8	2.6	2.52
$Li_{0.2}Zn_{0.8}WO4$	50.7	9.5	2.41

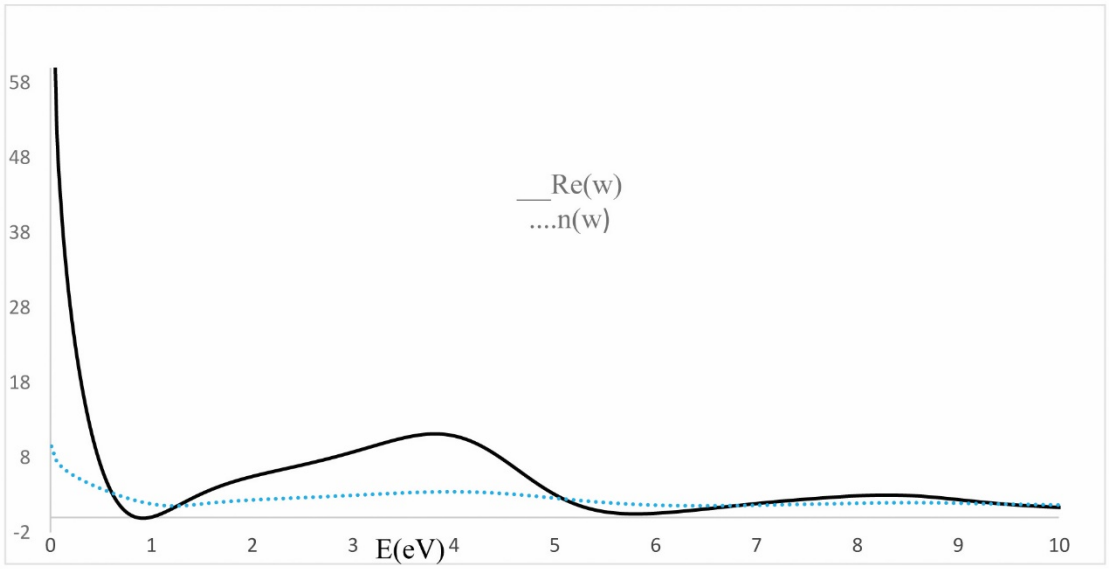

Fig 2: The real part of the dielectric function and refractive index of Li-ZnWO4

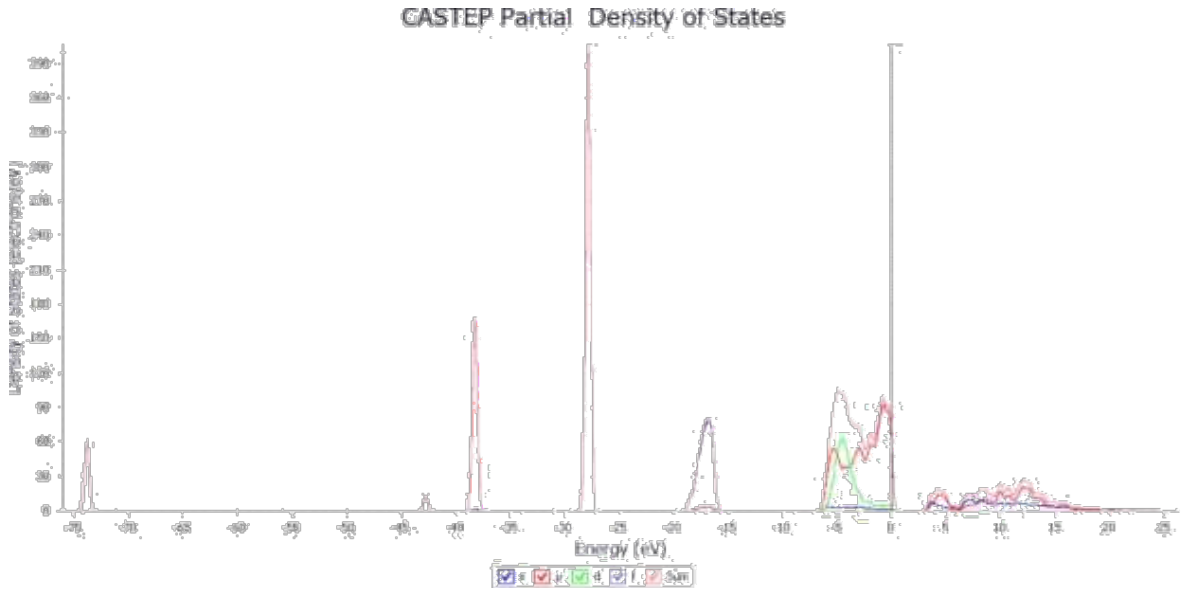

Fig 3: the total density states (TDOS) and partial density states (PDOS) of Li- ZnWO4

To reveal the distinction of optical properties caused by the intrinsic structure of the materials, the total density of states (TDOS) and partial density of states (PDOS) of were also studied and are shown in Figure 3. It is remarkable that the upper VB of pristine $ZnWO_4$ is predominantly formed by O 2p and Zn 3d states, and the conduction band consists of O 2p and Zn 4s states. The W element in ZWO has the electron density of states in the deep VB, but no electron density near the Fermi level, indicating that the W element has a negligible contribution to the band structure of ZnWO4 doped.

Conclusion

Density functional theory (DFT) calculations were further conducted, revealing that the introduction of Li can narrow the band gap of $ZnWO_4$. According to the energy gap, we find that at first energy gap decreases by increasing Li. Also, dielectric constant and static refractive index increase by Li increasing. In $ZnWO_4$ doped, new electron traps are inserted to the sample, causing more carriers to be trapped in the $Li_xZn_{1-x}WO4$ trap for delaying the recombination of the electron-hole pairs. When more electrons and holes are separated, the photocatalytic activity of Li doped $ZnWO_4$ will become higher. $ZnWO_4$ doped can be used for sewage treatment.

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