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## **Augmented the Structure, Electronic and Optical Characteristics of PEO Doped NiO for Electronics Applications**

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This paper aims to investigate the structural, optical and electrical properties of PEO doped with NiO. The DFT calculations have been performed using Gaussian 09 package of programs. The calculated electronic properties included the total energy, HOMO and LUMO energies, energy gap, ionization energy, electron affinity, electronegativity, electrochemical hardness, electronic softness and electrophilic index. The obtained results showed that the doping PEO with NiO improved the structural, optical, electronic and electrical characteristics where the energy band gap decreases about 67.4 % with addition of NiO which make the (PEO-NiO) composites are promising materials for flexible optoelectronics fields in the development of electronics applications.

**Keywords:** PEO, NiO, DFT, optical properties, electronics devices, Gaussian 09.

*Received 18 June 2021; Accepted 30 August 2021.*

### **Introduction**

Nanocomposites of organic and inorganic semiconductors dispersed in polymer matrices are multifunctional materials often suggested as elements of nonlinear optical devices and for development of plastic solar cells. The increasing interest in their possible use is caused by their plasticity, simple preparation techniques, and an opportunity to tune their properties by changing the concentration and the nanoparticle size in the matrix. A polymeric nanocomposite should possess high optical and photochemical stability [1]. Ceramic materials are typically brittle, possess low dielectric strength and in many cases are difficult to be processed requiring high temperature. On the other hand, polymers are flexible, can be easily processed at low temperatures and exhibit high dielectric break down fields [2]. Polymers are considered a good choice as host materials, because they normally exhibit long-term stability and possess flexible reprocessability and they can be designed to yield a variety of bulk physical properties. This new class of organic inorganic composites or hybrid materials may afford potential applications in molecular electronics,

photoelectrochemical cells, optics, solvent-free coatings, etc [3]. Organic polymers show ample evidence of optical, electronic and optoelectronic properties and are at length used in optical devices like lenses, optical waveguides, optical switches, light emitting diodes and nonlinear optical applications extended use of optical polymers, it is therefore advantageous to have polymers with a property, like refractive index, within a certain range [4]. Polyethylene oxide (PEO) is a linear and semi-crystalline polymer. Because PEO is a linear polymer, the regularity of structure unit permits a high crystallinity degree. The chemical structure of PEO contains of polar group –O– that can interact/associate with the cations of metal salt. Thus, PEO can solvate different types of salts. However, the reactivity is very low because of its structural unit has C–H, C–C, C–O bonds. Due to this, it is stabilized chemically and electrochemically. But, a high concentration of crystalline phase within PEO polymer confines the conductivity[5]. This work aims to design of PEO/NiO structures and investigating the structural, optical and electronics properties to use in different optoelectronics and electronics devices.

## I. Theoretical Part

The energy gap is calculated by the following formula[6-9]:

$$E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}}, \quad (1)$$

where  $E_g$  is the energy gap,  $E_{\text{LUMO}}$  is the energy of the low unoccupied molecular orbital,  $E_{\text{HOMO}}$  is the energy of the highest occupied molecular orbital.

The total energy is the summation of total kinetic and potential energy, at the optimized structure where the total energy of the molecule must be at the lowest value due to the molecule is at the equilibrium position, which means, the of the effective forces is zero [10]. The ionization energy is expressed by the equation[11]:

$$I_E = -E_{\text{HOMO}} \quad (2)$$

Electron affinity can be given as the energy released when an electron bonds to an atom or molecule resulting in the formation of a negative ion [12].

$$E_A = -E_{\text{LUMO}} \quad (3)$$

The chemical potential ( $\mu$ ) is measured the escaping tendency of electronic cloud which is given by[13]:

$$\mu \approx \frac{1}{2}(E_{\text{HOMO}} + E_{\text{LUMO}}) \approx -\frac{1}{2}(I_E + E_A), \quad (4)$$

Chemical hardness is calculated by [14]:

$$H = \frac{I_E - E_A}{2} \quad (5)$$

Chemical softness  $S$  is the inverse with hardness as the following equation[15]:

$$S = \frac{1}{2H} \quad (6)$$

Electrophilicity is defined by the equation [16]:

$$\omega = \frac{\mu^2}{2H} \quad (7)$$

R. Mulliken defined electronegativity as the following[17]:

$$E_N = \frac{1}{2}(I_E + E_A) \quad (8)$$

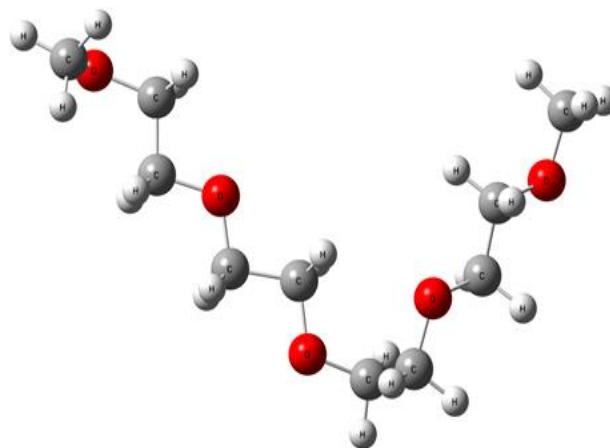
The electric dipole polarizability is the measure of the linear response of the electron density in the presence of an infinitesimal electric field  $F$  and it represents a second order variation in energy [18]. The polarizability is calculated by the following equation [19].

$$\langle \alpha \rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (9)$$

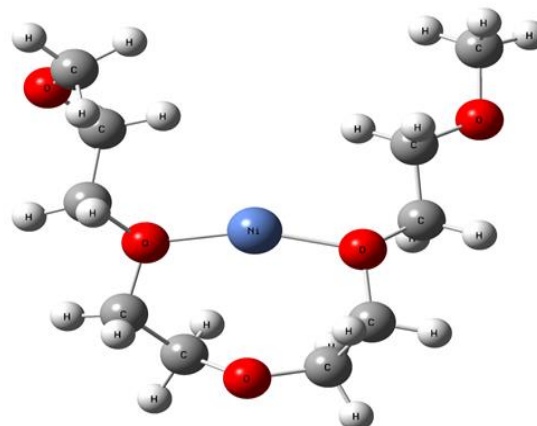
## II. Results and Discussion

Geometry optimization is a standard chemistry-physical calculation to find the lowest energy or largest

relaxed conformation for a molecule, it is performed by find the first derivative of the energy with respect to distance between different atoms, known as the gradient, at the stationary point this gradient is zero, since the gradient is the negative of the force, the forces are also zero at such point. The optimization structures of the pure (PEO), (PEO-NiO) nanocomposites, are seen in Figs. 1, 2. The optimized parameters of these molecules encompassed bonds in ( $\text{\AA}$ ) and angles in ( $^\circ$ ) calculated from DFT-B3LYP/6-31G are shown in Table 1.



**Fig.1.** Optimization of PEO structure.

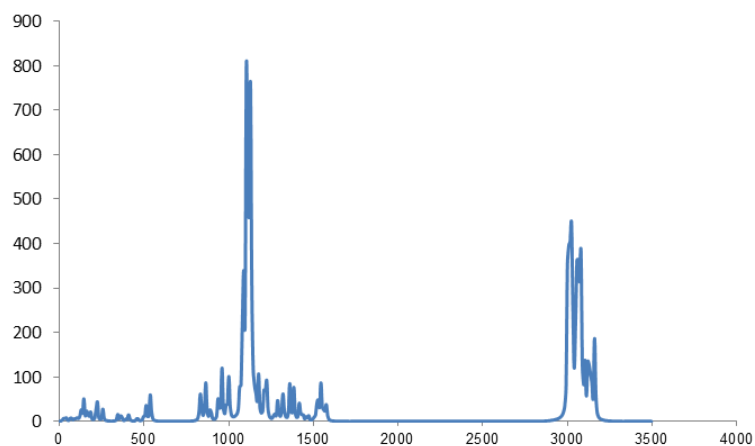


**Fig.2.** Optimization of (PEO-NiO) structures.

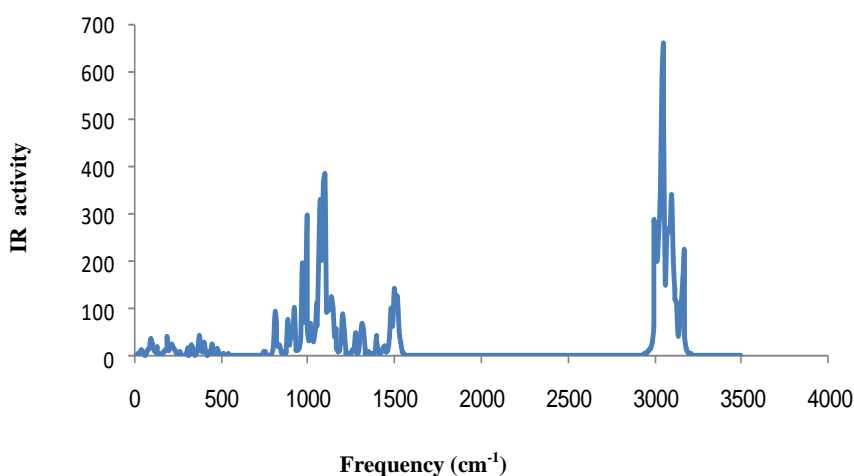
**Table 1**

Average lengths of bond in ( $\text{\AA}$ ) and the angles in degree

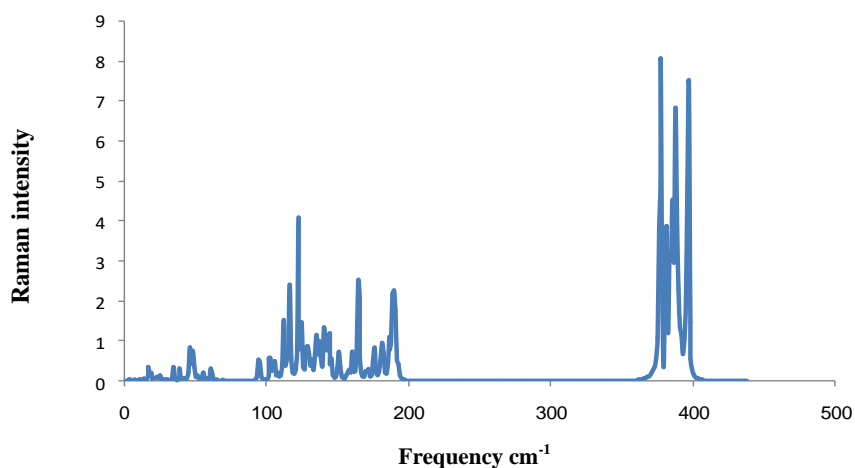
Measurements	The optimization parameters	Values
Bonds $\text{\AA}$	( C-C )	1.52609
	( C-O )	1.45350
	( C-H )	1.09983
	( O-H )	1.056
	( NI-O )	1.89952
Angles Deg.	( C-O-C )	33.45179
	( O-C-H )	111.40754
	( H-C-H )	108.79899
	( H-H-H )	35.76269



**Fig. 3.** IR spectra of (PEO) structure.



**Fig. 4.** IR spectra of (PEO-NiO) structure.



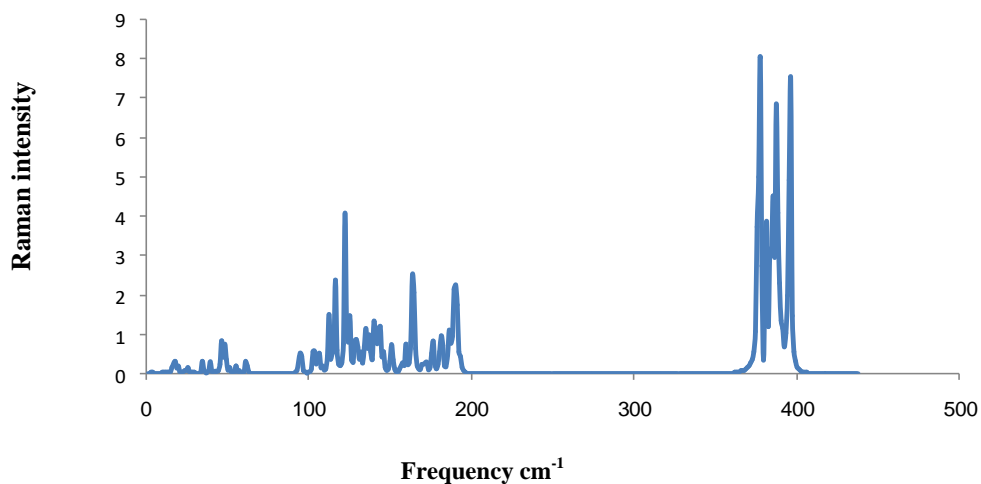
**Fig. 5.** Raman intensities of (PEO) structures with vibration frequency.

The optimized structure for the pure PEO and nanocomposites in this work the structures are initially designed at Gauss View 5.0.8 program, and relaxed at Gaussian 09 package of programs by employing B3LYP/6-31G for PEO and SDD for nanocomposites.

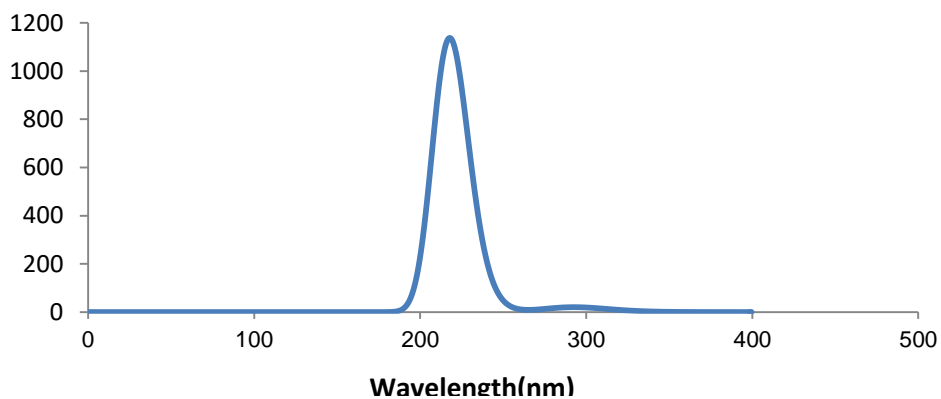
Figures (2) and (3) show the IR-Spectrum of (PEO)

and (PEO-NiO) structures using density functional theory. It was noted that the strong peak of (PEO-NiO) structures observed at (3048 $\text{cm}^{-1}$ ).

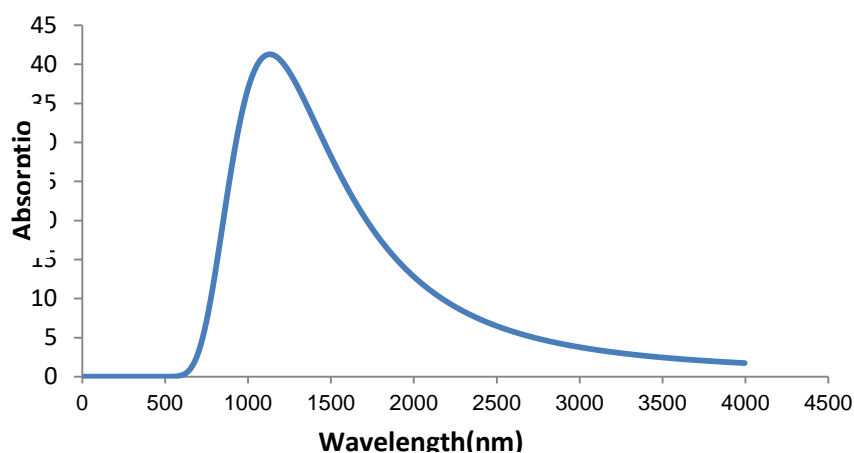
Figures (7) and (8) show the UV-Vis spectra Visible and Ultra Violet spectrum is dependent on upon the electronics structure of the molecule. The UV-Vis



**Fig. 6.** Raman intensities of (PEO-NiO) structures with vibration frequency.



**Fig. 7.** UV-Vis spectrum for (PEO) structure.



**Fig. 8.** UV-Vis spectrum for (PEO-NiO) structures.

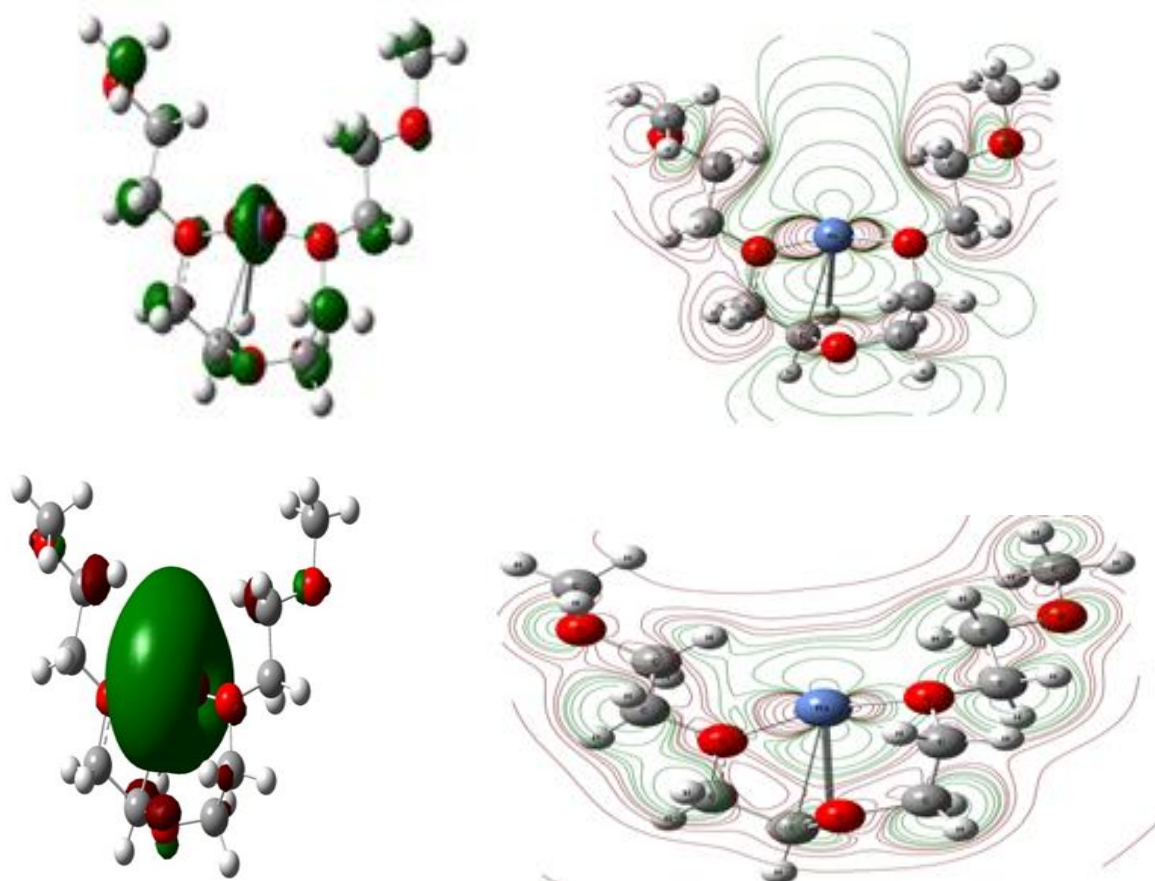
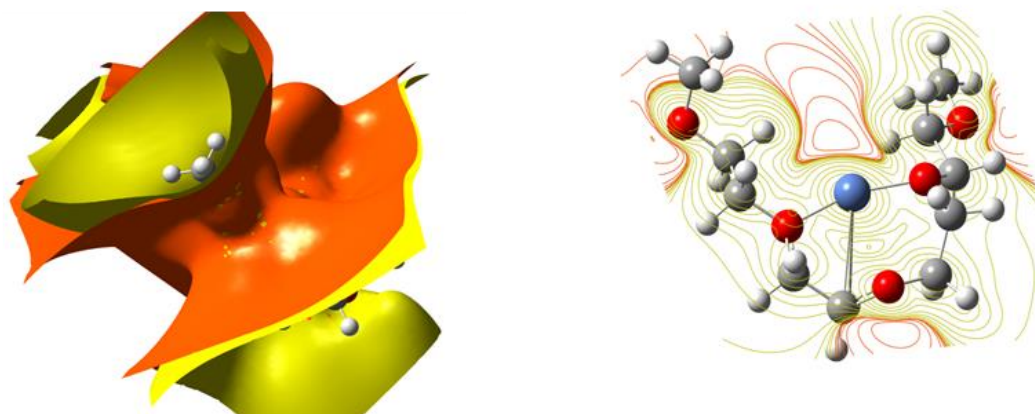
calculations of the (PEO) and (PEO-NiO) structures which get by the B3LYP-TD/SDD method included the excitation energy, wavelength, oscillator strength and electronic transition.

Table 2 represents the comparison between  $E_g$  values of (PEO),(NiO) and (PEO-NiO) structures, then compared with the Refs. [20 and 21]. Figures(8)

illustrates the 3-D distribution of HOMO<sup>s</sup> and LUMO<sup>s</sup> for the (PEO-NiO) structures. The HOMO–LUMO visualization obviously characterizes the cloud of electron in virtual and occupied orbitals. The green color represents the molecular orbital of highest energy HOMO while red color represents the molecular orbital of lowest energy LUMO in the structures. The energy

**Table 2**

Energy gap values of structures								
PEO			NiO			(PEO-NiO)		
$E_{HOMO}$ (eV)	$E_{LUMO}$ (eV)	$E_g$ (eV)	$E_{HOMO}$ (eV)	$E_{LUMO}$ (eV)	$E_g$ (eV)	$E_{HOMO}$ (eV)	$E_{LUMO}$ (eV)	$E_g$ (eV)
-6.4811	1.6587	8.1398	-6.5807	-4.5497	2.031	-2.8064	-0.1548	2.6516


**Fig. 9.** The distribution of HOMO(up) and LUMO(down) (PEO-NiO) structures.

**Fig. 10.** Electrostatic potential distribution surface for (PEO-NiO) structures.

band gap of PEO decreases with adding of NiO, this behavior due to increase of the localized level in energy gap [22-30], which make it suitable in many optoelectronics applications.

Figure 10 illustrates the electrostatic surfaces potential distribution of structures calculated from the total self-consistent field (SCF). ESP distributions of structure are created by repulsive forces or by attracting

**Table 3**

Electronic properties values in eV of the structure

Property	NiO	PEO	(PEO-NiO) structure
Total energy	-244.3948	-770.1046	-941.1620 (a.u)
Ionization potential	6.5807	6.4811	2.8064
Electron affinity	4.5497	-1.6587	0.1548
Electronegativity	5.5652	2.4112	1.4806
Chemical hardness	1.0155	4.0699	1.3258
Chemical softness	0.4923	0.1228	0.3771
Chemical potential	-5.5652	-2.4112	-1.4806
Electrophilicity	15.2491	0.7142	0.8267
Dipole moment (Debye)	4.587	1.8044	1.7125

regions around each structure.

Table 3 shows the results of the  $E_T$  in a. u and some electronic characteristics of (PEO),(NiO) and (PEO-NiO) structures calculated at the same level of theory. These properties are included IE, EA,  $E_N$ , H and  $\omega$ .

Table 4 shows the polarizability average  $\alpha_{ave}$  and it is components in a.u of (PEO-NiO) structures.

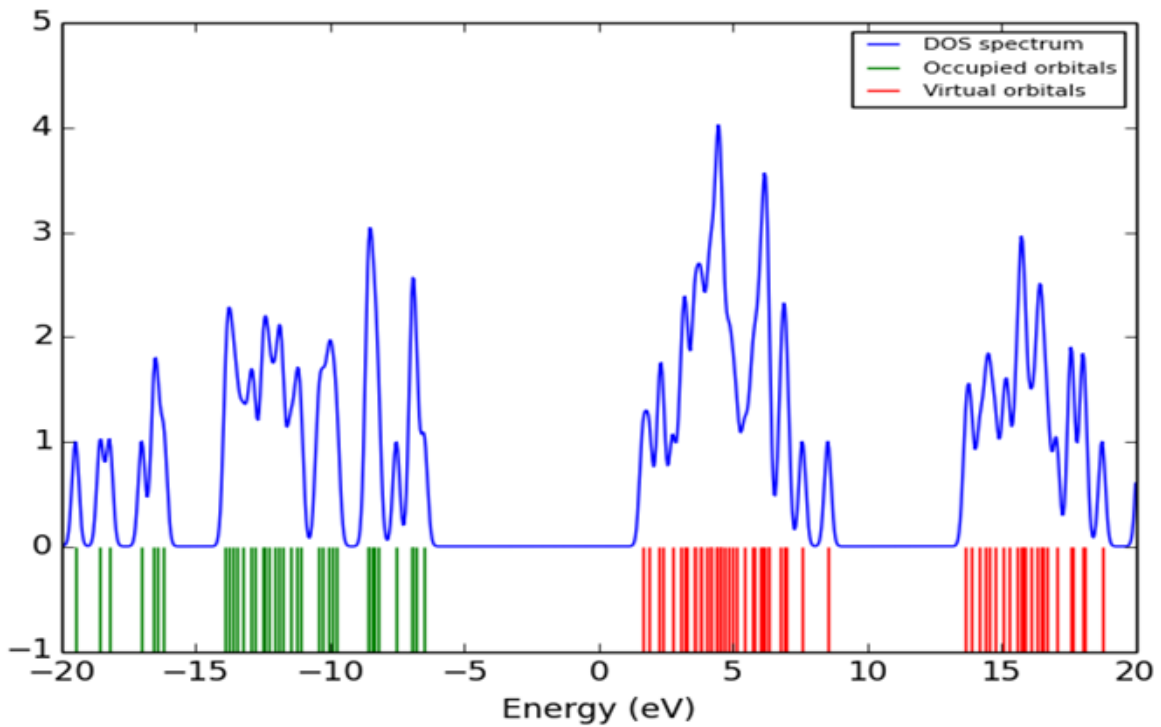
The strength of interactions can be further studied by analyzing orbital interactions between the atoms of nanocomposite, in terms of density of statesDOS. The DOS governs many physical properties and consequently plays an important role in solid state physics, it is important to be able to predict how the DOS will behave for different molecular structures geometries.

The density of states of (PEO) and (PEO-NiO) structures with energy levels were calculated by employing the DFT-B3LYP/SDD level of theory as presented in Figures 11 and 12 Density of states (DOS) spectrum.

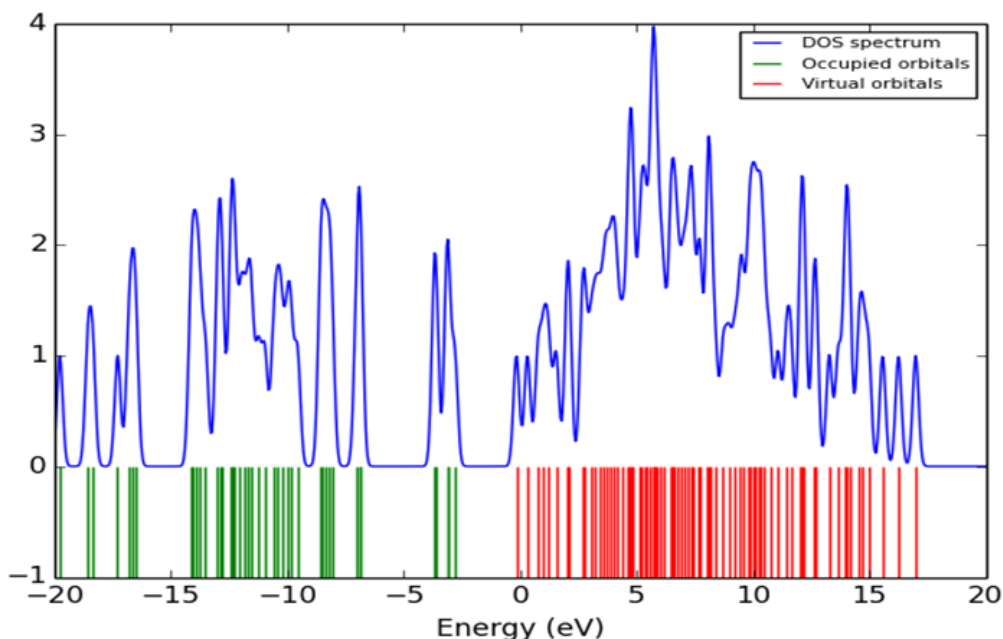
**Table 4**

The calculated  $\alpha_{ave}$  and it is components of (PEO-NiO) structures

Polarizability(a.u)			
$\alpha_{xx}$ (a.u)	$\alpha_{yy}$ (a.u)	$\alpha_{zz}$ (a.u)	$\alpha_{ave}$ (a.u)
189.476	194.930	156.744	180.383



**Fig. 11.** DOS of (PEO) structure.



**Fig. 12.** DOS of (PEO-NiO) structures.

## Conclusions

This work includes the investigating the structural, optical and electrical properties of PEO doped with NiO. The DFT calculations have been performed using Gaussian 09 package of programs. Density functional theory calculations are used to study the optimized and simulated of (PEP-NiO) structures by using B3LYP/SDD basis set. The structural, optical, electronic and electrical characteristics of PEO were enhanced with adding of

NiO. The energy band gap decreases about 67.4 % with addition of NiO which make the (PEO-NiO) composites are promising materials for flexible optoelectronics fields in the development of electronics applications. The final results showed the PEO/NiO structures can be used in different renewable and electronics applications.

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- [1] P. Lutsyk, L. Dzura, A. Kutsenko, Ya. Vertsimakha, J. Sworakowski, *Quantum Electronics & Optoelectronics* 8(3), 54 (2005); <https://doi.org/10.15407/spqeo8.03.054>.
- [2] S. Devikala, P. Kamaraj and M. Arthanareeswari, *Chem. Sci. Trans.* 2(S1), S129 (2013); <https://doi.org/10.7598/cst2013.26>.
- [3] I.R. Agool, K.J. Kadhim, A. Hashim, *International Journal of Plastics Technology* 21(2), (2017), <https://doi.org/10.1007/s12588-017-9192-5>.
- [4] K. Das, P. Pendke and J.M. Keller, *Research Journal of Recent Sciences* 5, 79 (2016).
- [5] El. Metwally M. Abdelrazek, Amr M. Abdelghany, Shalabya I. Badr, Mohamed A. Morsi, *J. mater. Res. Technol.* 7(4), 419 (2018); <https://doi.org/10.1016/j.jmrt.2017.06.009>.
- [6] P. Chen, *Qualitative MO Theory and Its Application to Organic Reactions, Thermal Rearrangements, Pericyclic Reactions* (ETH Zurich, SS, Zurich, 2005).
- [7] J. Simons, *An introduction to theoretical chemistry* (Cambridge University Press, 2003).
- [8] D. Marx, & J. Hutter, *Modern methods and algorithms of quantum chemistry* 1(301-449), 141 (2000).
- [9] H. Dorsett, & A. White, *Overview of molecular modelling and ab initio molecular orbital methods suitable for use with energetic materials* (Defence science and technology organization Salisbury, Australia, 2000).
- [10] I.N. Levine, D.H. Busch, & H. Shull, *Quantum chemistry* (Vol. 6) (Upper Saddle River, NJ: Pearson Prentice Hall, 2009).
- [11] H.M. Kampen, H. Méndez, & D.R.T. Zahn, *Energy Level Alignment at Molecular Semiconductor/GaAs (100) Interfaces: Where is the LUMO* (University of Chemnitz, Institut fur, Germany, 1999).
- [12] M.J. Frisch, & F.R. Clemente, *Gaussian 09, Revision A. 01*, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, GA Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zhe.

- [13] K. Sadasivam, & R. Kumaresan, Computational and Theoretical Chemistry 963(1), 227 (2011); <https://doi.org/10.1016/j.comptc.2010.10.025>.
- [14] O.A. Kolawole, & S. Banjo, Theoretical Studies of Anti-corrosion Properties of Triphenylimidazole Derivatives in Corrosion Inhibition of Carbon Steel in Acidic Media via DFT Approach. (2018).
- [15] P.W. Atkins, & R.S. Friedman, Molecular quantum mechanics (Oxford university press, 2011).
- [16] V. Subramanian, Quantum Chemical Descriptors in Computational Medicinal Chemistry for Chemoinformatics. Central Leather Research Institute, Chemical Laboratory, 0-0000. (2005).
- [17] L. Shenghua, Y. He, & J. Yuansheng, International Journal of Molecular Sciences 5(1), 13 (2004); <https://doi.org/10.3390/i5010013>.
- [18] A.J. Camargo, K.M. Honório, R. Mercadante, F.A. Molfetta, C.N. Alves, & A.B. da Silva, Journal of the Brazilian Chemical Society, 14(5), 809 (2003); <https://doi.org/10.1590/S0103-50532003000500017>.
- [19] P. Udhayakala, & T.V. Rajendiran, Journal of Chemical, Biological and Physical Sciences (JCBPS) 2(1), 172 (2011).
- [20] S.X. Tao, A.M. Theulings, J. Smedley, & H. van der Graaf, Diamond and Related Materials 58, 214 (2015); <https://doi.org/10.1016/j.diamond.2015.08.005>.
- [21] V. Nagarajan, Saravanakannan Venkatesan, R. Chandiramouli, International Journal of ChemTech Research, 6(14), 5466 (2014).
- [22] Aseel Hadi, Ahmed Hashim, Yahya Al-Khafaji, Transactions on Electrical and Electronic Materials 21, (2020); <https://doi.org/10.1007/s42341-020-00189-w>.
- [23] Ahmed Hashim, J Mater Sci: Mater Electron, (2021); <https://doi.org/10.1007/s10854-020-05032-9>.
- [24] H.H. Khalid, Al-Attayah, Ahmed Hashim, Sroor Fadhil Obaid, International Journal of Plastics Technology 23(1), (2019); <https://doi.org/10.1007/s12588-019-09228-5>.
- [25] Ahmed Hashim, Yahya Al-Khafaji, Aseel Hadi, Transactions on Electrical and Electronic Materials 20, (2019); <https://doi.org/10.1007/s42341-019-00145-3>.
- [26] Qayssar M. Jebur, Ahmed Hashim, Majeed A. Habeeb, Structural, Transactions on Electrical and Electronic Materials (2019); <https://doi.org/10.1007/s42341-019-00121-x>.
- [27] Ahmed Hashim, Enhanced Structural, Journal of Inorganic and Organometallic Polymers and Materials 30, (2020); <https://doi.org/10.1007/s10904-020-01528-3>.
- [28] Ahmed Hashim, Zinah S. Hamad, Egypt. J. Chem. 63(2), (2020); <https://doi.org/10.21608/EJCHEM.2019.7264.1593>.
- [29] A. Hashim, K.H.H. Al-Attayah, S.F. Obaid, Ukr. J. Phys. 64(2), (2019); <https://doi.org/10.15407/ujpe64.2.157>.
- [30] Ahmed Hashim, Journal of Inorganic and Organometallic Polymers and Materials 31, (2021); <https://doi.org/10.1007/s10904-020-01846-6>.

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## Доповнення структурних, електронних та оптичних характеристик РЕО легованих NiO для застосувань в електроніці

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Стаття спрямована на дослідження структурних, оптичних та електричних властивостей РЕО, легованих NiO. DFT розрахунки виконано за допомогою програмного пакету Gaussian 09. Обчислені електронні властивості включали повну енергію, енергії НОМО та LUMO, ширину забороненої зони, енергію іонізації, спорідненість електронів, електронегативність, електрохімічну твердість, електронну м'якість та електрофільний індекс. Отримані результати показали, що легування РЕО з NiO покращило структурні, оптичні, електронні та електричні характеристики, де ширина забороненої зони зменшується приблизно на 67,4 % із додаванням NiO, що робить композити (РЕО-NiO) перспективними матеріалами для гнучких оптоелектронних пристроїв.

**Ключові слова:** РЕО, NiO, DFT, оптичні властивості, електронні пристрої, Gaussian 09.