UNIVERSITI TEKNOLOGI MARA

FIRST-PRINCIPLES STUDY ON STRUCTURAL, ELECTRONIC AND OPTICAL PROPERTIES OF Ln-DOPED Bi_2O_3 (Ln = Eu, Gd AND Er) AS A PHOTOCATALYST

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MSc

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AUTHOR'S DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the results of my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any degree or qualification.

I, hereby, acknowledge that I have been supplied with the Academic Rules and Regulations for Post Graduate, Universiti Teknologi MARA, regulating the conduct of my study and research.

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ABSTRACT

Crystal structures of α-Bi_2O_3 and β-Bi_2O_3 were calculated using Cambridge serial total energy package (CASTEP) based on the first-principles plane-wave ultrasoft pseudopotential method within local density approximation (LDA) and generalized gradient approximation (GGA) together with Perdew–Burke–Ernzerhof (GGA-PBE) and Perdew–Burke–Ernzerhof revised for solid (GGA-PBEsol). The structural parameter of α-Bi_2O_3 and β-Bi_2O_3 are in good agreement with previous experimental and theoretical data (Matsumoto, Koyama, Tanaka 2010). The DFT+U method gives the correction due to the underestimate results from DFT as compared to the experimental value. All of the polymorphs were calculated for the total density of states (TDOS) and the partial density of states (PDOS) of Bi, O atoms. Density of states exhibits hybridization of Bi 6*s* and O 2*p* orbitals and the calculated charge density exhibit the ionic character in the chemical bonding of this compound. The narrowed band gap (E_g) and red shift of light absorption edge are responsible for the photocatalytic activity of β-Bi_2O_3 for water splitting application. β-Bi_2O_3 is the best structure among these polymorphs for the photocatalyst application based on the calculated optical properties such as optical absorption and electron energy loss function. Hence, β-Bi_2O_3 polymorph was used in the modification of Bi_2O_3 by doping method. Lanthanide (Ln) elements; Europium (Eu), Gadolinium (Gd) and Erbium (Er) as Ln dopants were determined. The Eu- and Gd-doped Bi_2O_3 were observed to have lower band gaps compared to pure Bi_2O_3. The band gap of Er- Bi_2O_3 was slightly higher than pure Bi_2O_3 but it can be related to the results of the absorption coefficient. The presence of Ln 4*f* states in Ln-doped Bi_2O_3 can be seen from the Density of States (DOS) which explained the narrowing of the band gap. Among the Ln-doped Bi_2O_3 (Ln = Eu, Gd and Er), the shifting of light towards a longer wavelength spectrum is obtained from the Gd-doped Bi_2O_3. Overall, the first-principles study in this work from the deepest level of atomic-scale can explain the law of physics from the properties of studied materials and improve the understanding of Bi_2O_3 semiconductor as a photocatalyst.

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