UNIVERSITI TEKNOLOGI MARA

FIRST-PRINCIPLES CALCULATIONS OF STRUCTURAL AND ELECTRONIC PROPERTIES OF MgO AND Li DOPED MgO

DZULKHAIRI TAJUDDIN BIN MUSTAFFA

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ABSTRACT

In this research, first principles calculation in CASTEP within density functional theory framework is used to study the structural properties and electronic properties of magnesium oxide (MgO). MgO has been observed to have its electronic properties to depend on its structural parameters. This work consist of three main parts, firstly the lattice parameters dependency of MgO towards its properties, the second part is the crystallite size dependency of MgO towards its properties and the third part is the lithium doping dependency of MgO towards its properties. For the first part, the lattice parameters that will be used in the calculation were obtained experimentally via X-ray Diffraction (XRD) of MgO. MgO structure that is used in this study is the face-centered cubic structure ($Fm\bar{3}m$) with space group of 225. From the calculated band structures, we have found that the decrease of MgO band gap is a consequence of the increase in lattice parameters and these findings agrees well with the experimental findings of band gap narrowing in MgO. The density of states of MgO is presented to study the shifting of the highest valence band and lowest conduction band. In the second part, the crystallite size dependency of MgO towards its structural properties and electronic properties is investigated. Two MgO structures were constructed on the basis of face centered cubic structure and the supercell method was implemented to construct MgO with 1x1x1 supercell and 2x2x2 supercell to simulate different crystallite size. From the calculations, as the crystallite size of MgO becomes smaller as simulated by MgO with 1x1x1 supercell, the lattice parameters of the MgO crystal increases. These finding proves the lattice expansion of MgO nanostructures. This lattice expansion is also the reason behind the band gap decrease of MgO which is agreeable with our findings from the first part of this work. The last part of this work is to study the doping effect of lithium in face centered cubic MgO. Initially, the stoichiometry of Li doped MgO is determined with two possibilities, which is the $Li_xMg_{1-x}O$ and $Li_{2x}Mg_{1-x}O$. The MgO structures were constructed with 2x1x1 supercell which consists of eight Mg atoms and eight O atoms and one lithium atom was inserted to replace one Mg atom in the 4a Wyckoff position to simulate the $Li_xMg_{1-x}O$ and in the second structure one lithium atom is inserted to replace one Mg atom in the 4a Wyckoff position and another lithium atom in the tetrahedral site; the MgO 2x1x1 to simulate the $Li_{2x}Mg_{1-x}O$ structure. From the energy calculated from both structures, it is found that $Li_{2x}Mg_{1-x}O$ electronic structure gives more accurate illustration of Li doped MgO. Three concentration of Li doping were studied which is x=0, 0.125 and 0.25 and it is found that as the Li concentration increases, the lattice parameters of Li doped MgO increases. The band gap of Li doped MgO decreases as the Li concentration increases. The density of states of Li doped MgO shows that Li creates a new energy level in the band structures of MgO promoting the decrease of band gap. The decrease of MgO band gap makes it viable for use in various electronic devices applications.

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CHAPTER ONE
INTRODUCTION

1.1 Background of Study

Nanotechnology is the engineering of functional systems at the molecular scale and is very diverse, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly and from developing new materials with dimensions on the nanoscale to direct control of matter on the atomic scale. Nanotechnology can also characterize, design and study the desired properties of materials for applications of the material for the specific applications with respect to the materials structure as well as functionalities. As the crystallite size of materials is reduced to nanoscale, a certain number of physical properties will also be altered with the change from macroscopic systems to low dimensional systems. One example is the quantum size effect where the electronic properties of solids are altered with great reductions in particle and/or crystallite size. For example nanoparticles take advantage of their dramatically increased surface area to volume ratio. Their optical properties, e.g. fluorescence, become a function of the particle diameter. This effect does not come into play by going from macro to micro dimensions. However, it becomes pronounced when the nanometre size range is reached.

One of the properties of materials that are studied by researchers in the advanced materials is the energy gap or band gap. Band gap is an energy range in a solid where no electron states can exist. In graphs of the electronic band structure of solids, the band gap generally refers to the energy difference (in electron volts) between the top of the valence band or highest occupied molecular orbital (HOMO) and the bottom of the conduction band or lowest unoccupied molecular orbital (LUMO) of the insulators and semiconductors. This is equivalent to the energy required to free an outer shell electron from its orbit about the nucleus to become a mobile charge carrier, able to move freely within the solid material. The band gap is therefore, a major factor in determining the electrical conductivity of a solid. Substances with large band gaps are generally insulators, those with smaller band gaps are semiconductors, while conductors either have very small band gaps or none at all, because the valence and conduction bands overlap. Band gap is one of the most useful feature of the band structure, as it strongly