UNIVERSITI TEKNOLOGI MARA

AB-INITIO STUDIES ON PROPERTIES OF STRAIN-FREE AND STRAINED PEROVSKITE-TYPE (ABO_3) MULTIFERROIC MATERIALS

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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

Multiferroic is one of the potential multifunctional materials for applications in novel based devices including magnetoelectric memory, spintronic and sensor. Efforts to develop more efficient multiferroic materials provide new opportunities and challenges in this field. Existing multiferroic materials were modified to enhance their existing properties. One of the known multiferroic materials is $BiFeO_3$ which has a great potential to exhibit excellent multiferroic properties at room temperature. In this work, the investigation focuses on the variety functional and physical properties of strain-free and strained perovskite-type multiferroic materials. The ab-initio calculations based on Density Functional Theory plus on-site Coulomb repulsion U method (LDA+U and GGA-PBEsol+U) as implemented in plane-wave pseudopotential CASTEP code were employed. The structural, lower energy symmetry, electronic, optical and elastic properties of strain-free $BiFeO_3$ were preliminary determined. It has been shown that the application of self-interaction corrected LDA+U and GGA-PBEsol+U functionals improve the accuracy of calculated properties. The results of structural, electronic, elastic and optical properties of $BiFeO_3$, calculated using LDA+U and GGA-PBEsol+U are in good agreement with other available calculations and experimental data. The lower energy symmetry of strained $BiFeO_3$ was then studied via ab-initio calculation. The calculation revealed that the possible structural phase transformation discovered in strained $BiFeO_3$ is due to the difference in volumetric strain effects. Moreover, misfit strain effects on the structural phase transformation, morphotropic phase boundary and physical properties of epitaxial $BiFeO_3$ thin film were further investigated. The major finding in this study reveals that the coexistence of rhombohedral-like and tetragonal-like phases in epitaxial $BiFeO_3$ thin film occurred at moderate compressive strain of in-plane *a*-lattice parameter, which is also in excellent agreement with recent experimental studies. The optical blue shifted in monoclinic phase and red shifted inpure tetragonal phase of epitaxial $BiFeO_3$ thin film were also discovered. Additionally, the modified $BiFeO_3$ was investigated by substituting the Bi (III) with La (III). The rhombohedral to orthorhombic phase transformation in $Bi_{1-x}La_xFeO_3$ solid solution was determined at x= 0.57 for rhombohedral *R3c* and orthorhombic *P21a* phases respectively, which are consistent with available experimental and other calculation studies. Furthermore, the novel perovskite-type materials based on lone pair $SbFeO_3$ and $BiVO_3$ compounds were successfully designed in this work using ab-initio computational method. It has been found that the most stable crystal structure of $SbFeO_3$ is antiferromagnetic monoclinic *Pc* phase. For $BiVO_3$, ferromagnetic monoclinic *P21/a* phase ($LaVO_3$-like structure) is found to be the most stable structure. These novel compounds have been found to demonstrate the structural phase transformation to polar monoclinic *Pm* and *Cc* phases under expansive volumetric strain effects. It is noted that the $BiVO_3$ and $SbFeO_3$ are metastable phase compounds under strain effect, which may be possible to be produced from high pressure-high temperature synthesis and epitaxial thin film growth techniques. Thus, the advanced epitaxial thin film growth technique is suggested as a potential method to synthesize $BiVO_3$ and $SbFeO_3$ single phase, which are promising candidates to be novel multiferroic materials.

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CHAPTER ONE
INTRODUCTION

1.1 BACKGROUND OF RESEARCH

In the last century, the rapid progress in materials science and technological instruments give a great impact to the society in term of the usage of electronic devices in daily lives. This impact thus increasing demands of the electronic devices and has attracted enormous attention of scientist and engineers to focus on the developing and designing new materials for advanced technology. This required an extensive investigation of materials properties from microscopic level with multidiscipline research areas such as solid-state physics, condensed matter, materials science and engineering as well as others. These investigations led to an advancement of technology such as sensor, memory, actuators and switches. These technologies are governed by the basic properties of the materials known as multiferroic [1-3]. Multiferroic is an (anti-)ferromagnetism and (anti-)ferroelectricity which coexisted in a pure phase material. This coexistence gives this material an ability to become a structural magnetic ferreolectrics (SMFs), which it can be interchangeably switched by applying the electrical and magnetic field [2, 4].

The most known structure of multiferroic is generally in the form perovskite structure. It is well known that in conventional perovskite-type ferroelectric materials (e.g. $BaTiO_3$, $PbTiO_3$ and $LiNbO_3$), empty electronic d^0 configuration [i.e. Ti (IV) and Nb (V)] is required for ferroelectricity. But, partial filled electronic d^n configuration [i.e. Fe (III), Mn (III) and Cr (III)] is required for magnetism. Thus, it seemed to preclude any coexistence of ferroelectricity and ferromagnetism. The other sources for ferroelectricity such as streochemically active lone pair of cations [i.e. 5s and 6s lone pair of valance electron in Pb (II) and Bi (III) cations], geometrical (size effects and geometric constraints) and electronic degree of freedoms (i.e. charge, spin and orbital) have been discovered in perovskite-type multiferroic. However, most of insulator perovskite-type multiferroic materials are in antiferromagnetic (AFM) ordering and