UNIVERSITI TEKNOLOGI MARA

FIRST PRINCIPLES STUDIES ON PROPERTIES OF Pb(II), Sn(II) AND Ge(II) FERROELECTRIC MATERIALS USING DENSITY FUNCTIONAL THEORY

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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

Quantum calculations via the first-principles study using the density functional theory (DFT) have offered great opportunities to describe the origin and most fundamental properties of new materials. In addition, detailed properties of the materials can be visualized by providing an accurate view at the atomic level. In this study, works are focused on investigating new lead-free ferroelectric materials that have a similar special ns^2 lone pair electrons with Pb (II) such as Sn (II) and Ge (II) via first principles calculation. Modification of Pb-based materials (PTO and PZT) by substituting or doping at the A-site are numerically anticipated to enhance the ferroelectric properties as well as to eventually reduce the consumption of Pb (II) in electroactive devices. Properties of lead-based materials $PbTiO_3$ (PTO), $PbZrO_3$ (PZO) and $PbZrTiO_3$ (PZT) as reference materials were compared with new lead-free ferroelectric materials such as $SnTiO_3$ (SnTO), $GeTiO_3$ (GTO) and $SnZrO_3$ (SnZO). All calculations were performed using first principles study based on Density Functional Theory (DFT) that has been implemented in CASTEP computer code. Functional GGA-PBEsol exhibits the most accurate values for lattice parameter with 0.6 % relative to experimental values for both cubic $PbTiO_3$ and $PbZrO_3$ (reference materials). Meanwhile, LDA-CAPZ functional is accurate for tetragonal PTO. The elastic properties values confirm that cubic PTO, SnTO, GTO, SnZO and PZO as well as tetroganal PTO, SnTO and GTO are mechanically stable. The electronic band structure, density of states (DOS) and electron density variation indicate the existence of hybridizations between anion O 2p and cation Pb 6s/Sn 5s/Ge 4s (special lone pair) in tetragonal PTO, SnTO, GTO and SnZO phase. Optical results show that anion O 2p, cation Pb 6p, Sn 5p , Ge 4p and Ti 3d, Zr 4d states respectively correspond to the transition electrons from valence states to the bottom of conduction state of the $ATiO_3$ (A=Pb, Sn, Ge) and $AZrO_3$ (A=Pb, Sn). The phonon calculation and cohesive energy revealed that the PTO and SnTO are stable in the tetragonal P4mm phase compared to the non polar ilmenite structure. However, $GeTiO_3$ apparently shows non-polar ilmenite structure is more stable compared to the ferroelectric perovskite structure. The phonon dispersion analyses for PZO and SnZO proves that both compounds have ground state structure with antiferroelectric orthorhombic (Pbam, no: 55 space group) and in approximation with the polar ferroelectric phase rhombohedral (R3c, no: 161 space group). In this work, calculations on novel compounds consist of Sn (II) and Ge (II) in PTO and Sn (II) in PZT provide new insights on geometrical and electronic structure of materials. Thus, these findings will be able to gear up efforts in reducing lead consumption by substituting or doping Sn and Ge in Pb-based system, and hence will substantially contribute to greener environment.

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CHAPTER ONE
INTRODUCTION

1.1 BACKGROUND

Rochelle Salt (RS) was the first material found to exhibit ferroelectric properties such as spontaneous polarization on cooling below Curie temperature (T_c), ferroelectric domain, and ferroelectric hysteresis loop (Brewster, 1824). Ferroelectric materials (ABO_3 type perovskite) are widely used in microelectronic industries. As such, the well-known Pb-based ferroelectric materials namely $PbTiO_3$ (PTO) and $PbZrTiO_3$ (PZT) are exploited in ultra-sensitive actuator, sensor, ultrasonic transducer and piezoelectric technologies (Noheda et al., 1999; Hosseini et al., 2007). The significance of these materials is due to their special chemical properties of Pb^{2+} cation in A-site of perovskite oxide. Besides that, their non-bonded lone pair $6s^2$ electrons are essential to provide a large polar displacement that introduces large elastic deformations and electric polarizations. However, total replacement of Pb-based materials in technological devices seems almost improbable because of inadequate performance of other materials. Thus, recent studies (Safari & Abazari, 2010; Bhandari et al., 2014; Vats et al., 2014) have extensively geared towards to identify new ferroelectric materials and other alternative compounds that are more environmental friendly and seeking for novel Pb-free ferroelectrics with cation displacements of comparable (or greater) magnitude for next-generation sustainable electroactive materials. However, modifications to reduce consumption of toxic Pb^{2+}, such as by substitution or doping techniques, are still necessary to be carried out.

Quantum calculations via the first-principles study using the density functional theory (DFT) have offered great opportunities to describe the origin and most fundamental properties of new materials. In addition, detailed properties of the materials can be visualized by providing an accurate view at the atomic level. Besides that, the first principles calculations require no empirical data and very cost effective compared to the experimental work, which eventually make the large-scale material designs more reasonable and affordable.