UNIVERSITI TEKNOLOGI MARA

FIRST-PRINCIPLES CALCULATIONS TO INVESTIGATE THE PROPERTIES TOWARDS LEAD-FREE TIN (II) AND LANTHANUM (III) DOPED LEAD ZIRCONATE TITANATE ($PbZr_{0.5}Ti_{0.5}O_3$) USING DENSITY FUNCTIONAL THEORY

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Thesis submitted in fulfillment
of the requirements for the degree of
Doctor of Philosophy
(Physics)

Faculty of Applied Sciences

May 2019

ABSTRACT

Lead-free elements based on Sn^{2+} and La^{3+} have been theoretically investigated as alternative materials for ferroelectric devices in PZT ($PbZrTiO_3$). The calculations were performed using first principles calculations based on Density Functional Theory (DFT) that has been implemented in CASTEP computer code. The doping of Sn^{2+} and La^{3+} in PZT is expected to enhance the ferroelectric performance of PZT. The geometry optimization of ferroelectric phase materials were calculated using different exchange correlation functional approximations namely Local Density Approximation (LDA-CAPZ) and Generalized Gradient Approximation (GGA-PBE, GGA-WC and GGA-PBEsol). GGA-PBEsol and LDA-CAPZ show the most accurate calculation values for lattice parameter and structure volume for PZT parent material viz. tetragonal PTO ($PbTiO_3$) and rhombohedral PZO ($PbZrO_3$). In addition, effects of La doped tetragonal PTO and rhombohedral PZO are also comparable with experimental results. Meanwhile, GGA-PBEsol and LDA-CAPZ functionals are accurate for tetragonal and monoclinic PZT, respectively. For PLZT ($PbLaZrTiO_3$), PLSnZT ($PbLaSnZrTiO_3$) and SnLZT ($SnLaZrTiO_3$) the most accurate function is GGA-PBEsol in tetragonal and monoclinic phase. The electronic band structure, density of states (DOS) and electron density indicate the existence of hybridizations among anion O 2*p*, cation Pb 6*s*/Sn 5*s* (special lone pair) and the Ti 3*d*/Zr 4*d* states of tetragonal PTO, SnTO ($SnTiO_3$), and rhombohedral SnZO ($SnZrO_3$) and PZO compounds as well as tetragonal and monoclinic PZT, PSnZT and SnZT. The hybridization of anion O 2*p*, cation Pb 6*s*/Sn 5*s*/ La 5*d* and the Ti 3*d*/Zr 4*d* also exists in PLTO ($PbLaTiO_3$), SnLTO ($SnLaTiO_3$), PLZT ($PbLaZrTiO_3$) and PLSnZT ($PbLaSnZrTiO_3$). The existence of Sn^{2+} and La^{3+} in PZT reduced the energy band gap that have consequently overcome the fatigue problem in PZT. The cohesive energy showed that the tetragonal P4*mm* phase of PTO and SnTO as well as rhombohedral phase PZO and SnZO are stable with the lowest energy at the ground state equilibrium structure. For tetragonal and monoclinic PZT, the introduction of Sn^{2+} in PZT (PSnZT and SnZT) systems increased the spontaneous polarization of PZT. Furthermore, the La doped PZT, PSnZT and SnZT have also surged the value of polarization. In this work, calculations on novel compound consist of Sn^{2+} and La^{3+} in PZT could provide new results on geometrical and electronic structure of materials. Thus, these findings will be able to assist experimentalist in reducing lead consumption by substituting or doping Sn^{2+} and La^{3+} in Pb-based system, and hence will extensively contribute to green technology.

ACKNOWLEDGEMENTS

Above all, I would like to express my highest gratitude to God Almighty, Allah S.W.T for endless blessings, providing me an opportunity to study in Universiti Teknologi MARA (UiTM) as well as for giving me capability and strength to complete my research.

First and foremost, I am indebted to my family who have been my backbone, especially to my late mother, Siti Ramlah binti Drahman, my supportive father, Hussin bin Mat Ali, my beloved wife, Habibati Dini binti Haji Othman along with my fellow siblings and in-laws. Secondly, I would like to sincerely acknowledge my entire supervisors, Dr. Mohamad Fariz Mohamad Taib, Prof. Ts. Dr. Muhd Zu Azhan Yahya, Assoc. Prof. Dr. Oskar Hasdinor Hassan and Dr. Muhamad Kamil Yaakob. Multiple thanks for the constructive critics, beneficial comments plus valuable advices.

Furthermore, it would not have been imaginable to compose this doctoral thesis without the help and support from these kind people around me namely, Dr Rosnah, Dr Fadhlul Wafi, Fairoz, Sazwan and the rest of Imadian. Highest appreciation for being open-minded to spend times for thorough discussion and for recommending numerous of useful tips. Likewise, Hazrie, Anum, Nadzirah, Ani, Syazwan, Mimi, Haziq and Sya deserve special mention for their affectionate friendship for the past few years until now. They have been journeyed with me through ups and downs in finalizing this paper work.

Last but not least, remarkable credits dedicated to the financial support from Ministry of Higher Education (MOHE) in terms of MyPhD, and other research grants from Ministry of Science, Technology and Innovation (MOSTI). Besides that, I extend my deepest recognitions to every individuals, groups, departments and institutions which contribute to the accomplishment of this research.

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CHAPTER ONE
INTRODUCTION

1.1 Background of Study

Technological advancement has greatly relied on the development of advanced materials. Based on main requirements of many users in technological applications such as ultra-sensitive actuator, sensor, ultrasonic transducer and piezoelectric have assisted in tailoring the device to be smaller, portable and high performance. These requirements motivated material scientists and engineers to produce new materials that could push further the capability of existing technologies. These existing technologies are fundamentally governed by several material properties, and among of it is ferroelectric [2]. Since the discovery of ferroelectricity in Rochelle salt crystal by Valasek [3], followed by the discovery of the ferroelectricity in ABO_3 perovskite in 1945, numerous new materials have successfully been designed for a variety of industrial and commercial applications such as high-dielectric constant capacitors, ferroelectric thin film memories, piezoelectric sonars, positive temperature coefficient sensors and switches [4].

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 [5]. As the study in ferroelectric progressing continuously, materials with perovskite-based structure was identified to be excellent ferroelectric and piezoelectric application. Materials such as $PbTiO_3$ (PTO), $PbZrO_3$ (PZO), $PbZrTiO_3$ (PZT) and $PbLaZrTiO_3$ (PLZT) are well-known Pb-based ferroelectric [5-6]. The role of Pb in this material had been long understood in terms of its Pb^{2+} electronic structure. This Pb^{2+} has a relatively large high-lying occupied 6*s* orbital and a relatively low-lying extended unoccupied 6p state as reported by previous researcher [7-10]. This is known as "polarizable lone pair" of Pb^{2+} even though it is actually due to the cross-gap hybridization between the occupied O 2*p* states and unoccupied Pb 6*p* states [8]. In general, PZT is a ferroelectric material with a Curie temperature decreases gradually with Zr concentration. It shows several different ferroelectric phases including large rhombohedral ferroelectric and tetragonal