UNIVERSITI TEKNOLOGI MARA

FIRST-PRINCIPLES STUDY ON STRUCTURAL, ELECTRONIC AND THERMOELECTRIC PROPERTIES OF BULK AND SURFACE (001) ATiO3 (A=Pb, Sn) USING DENSITY FUNCTIONAL THEORY (DFT)

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ABSTRACT

The electronic, phase stability, epitaxial strain, and thermoelectric properties of cubic (P3mm) and tetragonal (P4mm) structures of PTO and SnTO were investigated using density functional theory (DFT). Cubic and tetragonal structures within the GGA-PBE and GGA PBE-sol functional were applied in a pseudo-potential plane wave using the CASTEP computer code respectively. The results showed that the tetragonal PTO and SnTO have the lowest cohesive energy of -39.320 eV and -39.523 eV respectively. Cubic PTO has an indirect band gap of 1.691 eV and SnTO is 1.164 eV while in the tetragonal phase, the band gap value of PTO and SnTO is 1.703 eV and 1.016 eV, respectively. In the PTO structure, the bond between Pb and O is ionic in the tetragonal state, while there is strong hybridization between Ti-3d and O-2p, which is significant for ferroelectricity. It is shown that the tetragonal is the most stable structure since it has the smallest cohesive energy compared to other structures. The out-of-plane c-axis strain is shown to be largely oriented to PTO under large in-plane a-axis compressive strain. The effect of epitaxial strain proved the surface compatibility in thin film applications. It shows that PTO and SnTO are suitable for surface cleaving. The cubic PbO terminated surface in PTO has a band gap of 1.572 eV gap which is almost equivalent to the bulk structure which is 1.691 eV compared to the TiO2 terminated surface which is 1.366 eV. The type-I surface of SnTO has an indirect band gap of 1.159 eV, whereas the type-II surface has a band gap of 1.196 eV. PTO has emerged as a promising material for thermoelectric application. In this study, the underlying mechanism to improve the thermoelectric efficiency of ATiO3 were determined. The thermoelectric parameters of the designed surface structures have been obtained by using the Boltzmann transport equation approximation in the WIEN2K computer code. The properties of the structure, electronic, and thermoelectricity were calculated and analyzed. The surface (001) modification through the AO termination layer has increased the electrical conductivity, thus increasing the power factor. On the other hand, increasing the Seebeck coefficient, lowering the thermal conductivity and thermopower, improves the figure of merit. It is shown that the thermoelectric performance of surface (001) cubic SnTO is higher as compared to PTO making it interesting for lead-free materials in thin-film applications.

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TABLE OF CONTENTS