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Ceramics International 39 (2013) S297–S300

CERAMICS INTERNATIONAL

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First principles calculation on structural and lattice dynamic of $SnTiO_3$ and $SnZrO_3$

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Available online 13 October 2012

Abstract

The geometry optimization, density of state (DOS) and lattice dynamic (born effective charges (BEC) and phonon dispersion) of $SnTiO_3$ (STO) and $SnZrO_3$ (SZO) cubic are investigated via first-principles computational methods. The results of DOS show that effect of different B-site cation–(Ti 3d, Zr 4d) states play an important role in chemical interaction particularly in changing of covalency between O2p and cation Sn-5p in STO and SZO, respectively. The BEC calculation shows the anomalous contribution to the Sn charge for both compound STO and SZO beyond the nominal charge of +2. Moreover, the replacement of Ti in STO by Zr strongly modifies the B–O interaction, suppressing the involvement change in nature of the unstable modes of $SnZrO_3$. The results were compared and showed in good agreement with other calculated values using different methods.

Keywords: Paraelectric; Density of state; Lattice dynamic; Geometry optimization

1. Introduction

$SnTiO_3$ is one of the promising Pb-free material which has been recently investigated theoretically using first principles that disclosed having high dielectric constant and ferroelectric polarization [1–3]. However, preparing single-phase $SnTiO_3$ ceramics using conventional preparatory methods is difficult due to the disproportionate on of Sn^{2+} at high temperatures [4]. Therefore, to apply this material as a reality in ferroelectric or piezoelectric devices, some modifications such as substitution or doping of the A site with another new suitable perovskite compound are required. Based on the similarity in special lone pair ns^2 ($n=5$ for Sn and $n=6$ for Pb), it is anticipated that $PbTiO_3$ (PTO) and $PbZrTiO_3$ (PZT) are good candidates as a base for preparing new compounds that consist of Sn^{2+} which are eventually expected to be more environmental friendly material. Using ABINIT code package, Cohen and Ganesh [5] reported a novel compound of $Pb_{0.5}Sn_{0.5}ZrTiO_3$ (PSZT) which have much higher values of piezoelectric coefficients (about 4–5 times that of PZT), meanwhile Roy and Vanderbilt [6] revealed that strong ferroelectric properties could be obtained from double rock-salts $PbSnZrTiO_6$. In order to realize a novel compound of $Pb_{0.5}Sn_{0.5}ZrTiO_3$ (PSZT) for the future application, concise studies on theoretical basis of $SnTiO_3$ (STO) and $SnZrO_3$ (SZO) become a prerequisite. However, most of the reported theoretical studies are focused on physical properties in the ferroelectric phase (i.e., tetragonal phase with P4mm space group) of $SnTiO_3$ [1,2,4], but little has reported in cubic phase (i.e., cubic unit cell with Pm3m space group) [7,8]. Moreover, it is noted that most of the previous work [1–4] only report on using local density approximation (LDA). Recent theoretical studies [9,10], show that Wu and Cohen (WC) functional gives acceptable structural properties of ABO_3 ferroelectrics such as lattice constants,

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http://dx.doi.org/10.1016/j.ceramint.2012.10.081

phonon frequencies, BEC, etc. Therefore, based on Density Functional Theory (DFT), we are motivated to firstly report on the first principles theoretical simulation studies on STO and SZO by applying Wu and Cohen (WC) [11] generalized-gradient approximation (GGA). The calculation of structural parameters and lattice dynamic of STO and SZO in its paraelectric phase were carried out. The simulation was conducted using the Cambridge Serial Total Energy Package (CASTEP) computer code.

2. Computational method

The calculations of cubic STO and SZO properties were performed using DFT plane–wave pseudo-potentials implemented in the CASTEP computer code [12].The exchange-correlation energy function was evaluated within the generalized-gradient approximation (GGA) given by Wu and Cohen (WC) [11]. The electrons Sn (5s, 5p), Ti (3d 4s), Zr (4d, 5s) and O (2s 2p) were treated as in their valence state. This geometry optimization was performed with convergence of energy change per atom of less than 5×10^{-6} eV, residual force of less than 0.01 eV/Å, stress below 0.02 GPa, and displacement of atoms during the geometry optimization of less than 0.0005 Å. The plane–wave cut-off energy 380 eV was employed and all atoms were geometrically optimized. The Brillouin zone was sampled using the Monkhorst–Pack scheme with a $6 \times 6 \times 6$ k-point set To evaluate the lattice dynamic namely BEC and phonon dispersion, the calculations were carried out using the density functional perturbation theory (DFPT) with 550 eV cut-off energy.

3. Results and discussion

3.1. Structural and density of state (DOS) of cubic STO and SZO

The value of unit cell lattice parameter, volume and total energy of cubic STO and SZO from the geometry optimization calculation are listed in Table 1. Recently, the

Table 1
Calculated structural parameter (lattice constant (a_o in Å) and volume (V in Å^3) and total energy (E in eV) of cubic STO and SZO with Pm3m space group.

ABO_3	Method	a_o	V	E
$SnTiO_3$	CASTEP–DFT (GGA–WC) present work	3.91	59.69	−3010
	CASTEP–DFT (LDA–CAPZ) [7]	3.85	57.03	–
$SnZrO_3$	(CASTEP) DFT–GGA–WC present work	4.13	70.53	−2689

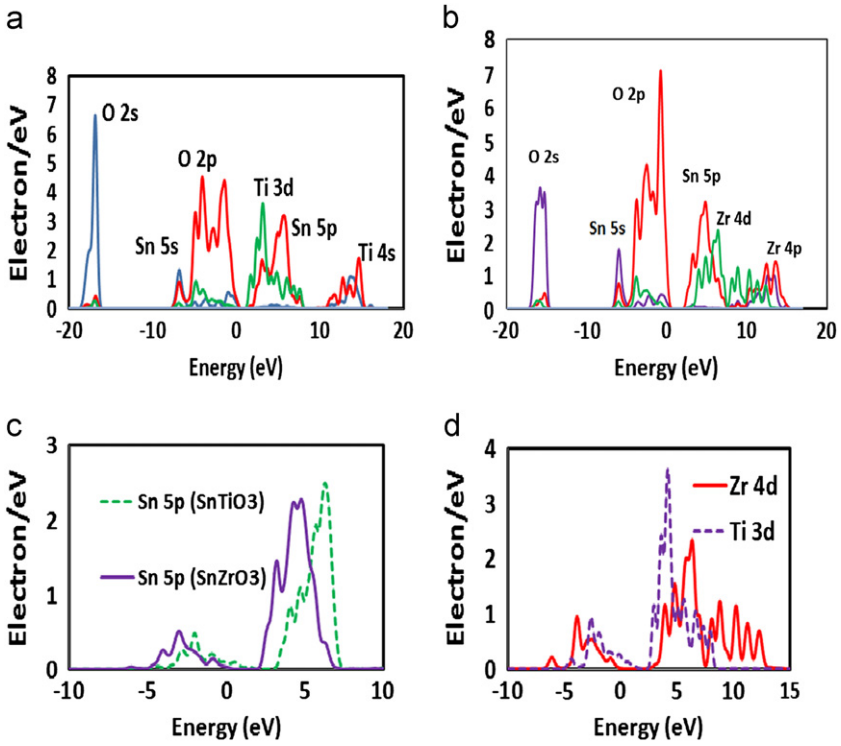

Fig. 1. Total DOS of cubic of (a) STO (b) SZO and partial DOS of (c) Sn 5p in STO and SZO (d) Ti 3d and Zr 4d in STO and SZO, respectively.

calculation of lattice parameter using GGA–WC [9,10] has shown to give accurate relative to the experimental values. The accuracy of the lattice calculation is very important because the change of 1–2% of the lattice will consequently affect the instability and other calculations of perovskite oxide. Therefore, it is a must to ensure that the lattice parameter used is reasonable, even though both the STO and SZO compound has no experimental values to compare with. The lattice parameters of STO and SZO are listed in Table 1. It can be observed that the volume of SZO is 18% higher than that of STO. As well known, the LDA calculation underestimates the lattice constant by 1–2% relative to experimental values. The present calculation of the lattice parameter and volume are acceptable and hence become a vital basis to further investigate on the properties of STO and SZO compound.

The total density of states (DOS) of STO (Fig. 1a) and SZO (Fig.1b) was calculated in order to understand the chemical bonding of the compound. Meanwhile, the effect of B-site (Ti/Zr) to the position of A-site cation Sn 5p state and also B-site cation Ti 3d and Zr 4d state in conduction band is shown in Fig. 1(c and d), respectively. The top valence band (VB) is dominated by O 2p (which has an approximate width of 6.5 eV) and also consists of Sn 5s states lying in the energy range −8.0 to 0 eV for $SnBO_3$ (B=Ti and Zr) compound.

Furthermore, it can also be seen that the lowest conduction band (CB) comprises of the Ti 3d and Zr 4d state; respectively, for STO and SZO compound. However, the conduction state has also strong contribution from Sn 5p state for both compound due to the hybridization between Sn 5p and O 2p. The results show that the hybridization of cation A site with anion O 2p (Sn 5p–O 2p) in SZO is enhanced compared to STO due to the different position of Sn 5p in STO and SZO (Fig. 1c). It can also be observed that there is a different position occurs between Zr 4d state (SZO) and Ti 3d state (STO) as shown in Fig.1(d). As a result, the strong covalency of Sn–O based on the lone pair ns^2 ($n=5$ for Sn) occurred, which might be as a key factor that affect the lattice dynamic such as BEC and perovskite stability (unstable mode in phonon dispersion will be discussed later).

3.2. Lattice dynamic

3.2.1. Born effectives charges (BEC) of cubic STO and SZO

The Born effective charge (BEC) Z* plays a crucial role in understanding the polar ground state and the lattice dynamics [13]. Calculated BECs for the cubic structure (Pm3m) of STO and SZO are listed in Table 2 and are compared with our pervious calculation [7] on the cubic STO using LDA with (1–6%) deviation. In the case of STO compound, Z*Ti (+6.91) and $Z^*O||$ (−5.76) are anomalously larger with respect to the nominal ionic charges of +4 for Ti and −2 for O. This can be best explained in terms of dynamic charges resulting from the hybridization between O 2p with Ti 3d which takes place along the Ti–O bond as the bond length is varied. However, the value of Z*B-site in Z*Zr cubic SZO (+6.47) and $Z^*O||$ (−5.19) decrease toward nominal charges with 6.4% and 11%; respectively, compared to that of STO. The Z*Sn in both materials are also significantly greater than its nominal charges of +2, which indicates that the bonding becomes more covalent in the Sn–O bond. The Z*Sn (+4.57) in STO is higher than that of Z*Sn (+4.49) in SZO by 1.75%. The $Z^*O_\perp$ (−2.89) in SZO is higher than $Z^*O_\perp$ (−2.87) in STO due to the strong covalency of Sn–$O_\perp$ in SZO compared to STO.

The present results are compared to the results obtained for another well-investigated of PTO and PZO [14], which predominantly have a covalent character because of their lone pair ns^2 ($n=5$ for Sn and $n=6$ for Pb) [15]. The covalent interaction tends to be a short range, while the ionic electrostatic interaction are long range and hence become an important key to study the instability of the compound. The interaction between A- and B-site cations with O in STO and SZO could be attributed to the anomalous Born effective charge and the instability of the perovskite mode that will be discussed in Section 3.2.2.

Table 3
Calculated frequency of phonon dispersion at the Γ and the lowest phonon frequencies at high-symmetry of Brillouin zone in the cubic phase of STO and SZO (cm^{-1}).

ABO_3	Method	TO1	TO2	T03	LO1	LO2	LO3
$SnTiO_3$	Present work	214i	188	587	62	344	747
	[7]	230i	139	718	54	262	809
$SnZrO_3$	Present work	228i	133	708	55	255	808
Lowest phonon frequency							
		Γ	X	M	R		
$SnTiO_3$	Present work	214i	127i	196i	201i		
$SnZrO_3$	Present work	228i	160i	235i	238i		

i=Imaginary part.

Table 2
Born effective charges of $SnTiO_3$ and $SnZrO_3$ compound in their cubic structure all the results compared with nominal charges (Z) of Sn=+2, Ti/Zr=+4 and O=−2.

ABO_3	Work	Z*A	Z*B	$Z^*O_\perp$	$Z^*O_{||}$	Z^*_A/Z_A	Z^*_B/Z_B
$SnTiO_3$	Present work	+4.57	+6.91	−2.87	−5.76	2.29	1.72
	[7]	+4.61	+6.55	−2.88	−5.39	2.31	1.64
$SnZrO_3$	Present work	+4.49	+6.47	−2.89	−5.19	2.25	1.62

3.2.2. Phonon dispersion of cubic STO and SZO

The instability of materials can generally be investigated via phonon dispersion. In particular, the presence of any unstable modes (i.e., an imaginary frequency in the dispersion curve below the zero frequency line) is important in evaluating the stability of the structure. The distortion mode of the perovskite oxide is affected by the ionic size of A- and B-site. LO (Longitudinal optical)–TO (Transverse optical) for the cubic structure of STO and SZO are listed in Table 3. Choice of functional (LDA or GGA–WC) influences the magnitude of the phonon frequency. The values of LO–TO splitting of STO in this work (GGA) deviate 1–45% from our previous report on STO using LDA [7] (see Table 3) and the report by Lebedev [8] using ABINIT computer code. The phonon dispersion calculation reveals the instability mode of this cubic crystal (STO). It is associated with X–R–M–Γ along high symmetry of Brillouin zone implying the most unstable mode is Γ_{15}, which competes with the unstable R_{25} and M_3 modes (see Table 3). The ferroelectric instability (polar distortion) is dominant in the cubic STO due to the unstable mode at Γ_{15} or TO1 ($-214\,cm^{-1}$). The results are comparable with other theoretical calculations [7,8]. From the analysis of gamma (Γ) point, the nature of the ferroelectric instability of the STO is expected to be very similar to that observed in STO investigated by Lebedev [8]. Therefore, the energetic considerations suggest that the most favorable ferroelectric phase of STO will be the tetragonal phase with P4mm space group. Meanwhile, the obtained phonon dispersion spectra of SZO show the unstable mode along X–R–M–Γ line symmetry as listed in Table 3. From phonon calculation, SZO exhibits the most unstable mode at R_{25} and M_3 mode. However, the unstable phonon mode also occurs at the Γ. This mode corresponds to the deformation of the oxygen octahedron and the ferroelectric distortions of the crystal structure are due to the lowest mode of phonon dispersion frequency along R_{25}, M_3 and Γ_{25} respectively. The nature of the structure instability of the SZO is obviously different compared to the STO perovskite oxide. This phenomenon occurs due to the covalency enhancement of Sn–O on SZO and this compound is energetically favorable to be distortions of octahedron rotation and then is lowered to I4/mcm or Pbnm. The results obtained are similar to $CdTiO_3$, $ZnTiO_3$ and $CaTiO_3$ that were reported by Lebedev [8]. In order to ensure whether SZO is an antiferroelectric or not (as shown in PZO system), an additional investigation is needed. Therefore, a deeper investigation of unstable phase of SZO will be carried out in future. This is to reconfirm the most favorable distortion of SZO either polar distortion (at Γ) or octahedron rotation (at R_{25} and M_3) influences within the structural optimization and ground state energy.

4. Conclusion

In this work, we provided an accurate structural optimization and the results DOS and BEC of STO and SZO. The covalency between Sn–O in comparable with Pb-based. The phonon analyses indicate that the distortion for STO is a polar rotation while SZO is an oxygen octahedral rotation. This interesting effort is focally geared to reduce lead consumptions by substituting or doping Sn in PZT system. It could substantially contribute to better green environment. Besides that, this finding will be able to play an important role in thoroughly providing a theoretical basis and thus could motivate experimental efforts to synthesis this material.

Acknowledgments

This work was supported by the Fundamental Research Grant Scheme by the Ministry of Higher Education, and Research Management Institute (RMI), Universiti Teknologi MARA, Malaysia.

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