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Novel high-K inverse silver oxide phases of SiO_2, GeO_2, SnO_2, and their alloys

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Abstract

The recently reported inverse silver oxide phase of SiO_2 possesses a high dielectric constant as well as lattice constant compatibility to Si. We explore the closely related oxides, GeO_2, SnO_2 with the same inverse silver oxide structure using ab initio density functional theory within the local density approximation (LDA). According to the phonon dispersion curves, both these structures are computed to be unstable. On the other hand, their alloys $Si_{0.5}Ge_{0.5}O_2$, $Si_{0.5}Sn_{0.5}O_2$, and $Ge_{0.5}Sn_{0.5}O_2$ are stable with higher dielectric constants than that of SiO_2 in the same phase. Their first-principles elastic constants, electronic band structures and phonon dispersion curves have been obtained with high precision.

Keywords: Ab initio electronical and structural calculation; Inverse Ag_2O (silver oxide) phase; High dielectric constant materials; Elastic properties

1. Introduction

The search for high-dielectric constant (high-K) oxides is proceeding in several fronts, such as the consideration of transitionmetal oxides like TiO_2, ZrO_2, and HfO_2. In the case of *crystalline* oxides, there is the additional possibility to search for advantageous polymorphs of the well-known oxides. Very recently, Ouyang and Ching [1] have reported a high-density cubic polymorph of SiO_2 in the inverse Ag_2O structure, named by them the "i-phase", possessing both high-K and lattice constant compatibility to Si(1 0 0) surfaces. For gate oxide applications, crystallization of high-K materials is in general undesirable since a poly-crystalline oxide will cause higher leakage currents and introduce new diffusion paths for dopants due to its grain boundaries [2]. On the other hand, a crystalline oxide grown epitaxially on Si can also be favorable as it will possibly result in a high interface quality. Particularly interesting would be a crystalline SiO_2 phase with a good lattice match to Si and a higher dielectric constant than that of amorphous SiO_2.

In this computational study, we continue this search for the crystalline high-K oxides with the i-phases of GeO_2 and SnO_2 as well as their ternary alloys including SiO_2. We employ the well-established ab initio framework based on the density functional theory within local density approximation (LDA) using pseudopotentials and a plane wave basis [3]. The mechanical stability of each material is checked using their computed elastic constants as well as with the phonon dispersion curves.

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2. Computational details

The simple cubic $X_{0.5}Y_{0.5}O_2$ polymorph in the inverse Ag_2O structure is shown in Fig. 1. The space group for the compounds, SiO_2, GeO_2 and SnO_2 is $Pn\bar{3}m$ and for their alloys $X_{0.5}Y_{0.5}O_2$ it becomes $P\bar{4}3m$. The structural and electronic properties of the i-phase structures under consideration have been calculated within the density functional theory [3], using the plane wave basis pseudopotential method as implemented in the ABINIT code [4]. The results are obtained under the LDA where for the exchange-correlation interactions we use the Teter Pade parameterization [5], which reproduces Perdew–Zunger [6] (which in turn reproduces the quantum Monte Carlo electron gas data of Ceperley and Alder [7]). We tested the results under two different norm-conserving Troullier and Martins [8] type pseudopotentials, which were generated by A. Khein and D.C. Allan (KA) and Fritz Haber Institute (FHI). In the course of computations, the plane wave energy cutoff and k-point sampling were chosen to assure a 0.001 eV energy convergence for all i-phase crystals. Phonon dispersions and phonon density of states (DOS) were computed by the PHON program [9] using a $2 \times 2 \times 2$ supercell of 48 atoms to construct the dynamical matrix. The required forces were extracted from ABINIT.

3. First-principles results

The lattice constants and other structural informations of all i-phase crystals are listed in Table 1.

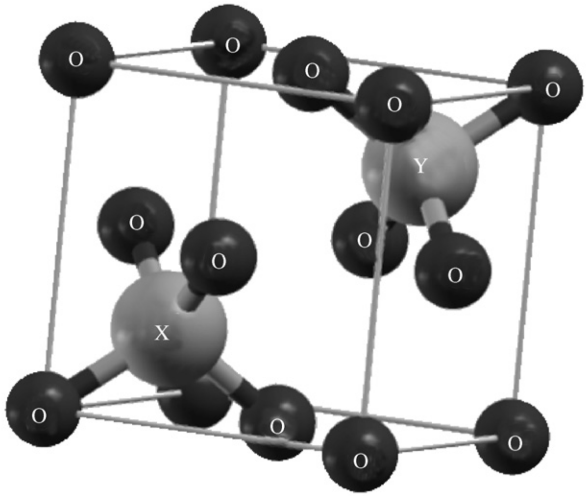

Fig. 1. Ball and stick model of $X_{0.5}Y_{0.5}O_2$.

Table 1
First-principles structural data for i-phase crystals

Crystal	a(Å)	Density (gr/cm^3)	X–O (Å)	Y–O (Å)
SiO_2	3.734	3.830	1.617	
GeO_2	3.916	5.781	1.696	
SnO_2	4.180	6.864	1.808	
$Ge_{0.5}Si_{0.5}O_2$	3.836	4.843	1.697	1.625
$Ge_{0.5}Sn_{0.5}O_2$	4.042	6.416	1.688	1.813
$Sn_{0.5}Si_{0.5}O_2$	3.970	5.590	1.818	1.620

Table 2
Elastic constants and bulk modulus for each crystal

Crystal	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	B (GPa)
SiO_2	383.6	260.0	243.0	301
GeO_2	297.0	231.2	175.6	253
SnO_2	208.9	185.5	113.9	193
$Ge_{0.5}Si_{0.5}O_2$	349.4	253.2	200.0	285
$Ge_{0.5}Sn_{0.5}O_2$	255.4	210.8	106.3	226
$Sn_{0.5}Si_{0.5}O_2$	277.5	217.4	103.9	237

Table 3
Dielectric permittivity tensor

Crystal	$\varepsilon^0_{xx} = \varepsilon^0_{yy} = \varepsilon^0_{zz}$	$\varepsilon^\infty_{xx} = \varepsilon^\infty_{yy} = \varepsilon^\infty_{zz}$
SiO_2	9.857	3.285
GeO_2	31.826	3.728
SnO_2	22.032	3.478
$Ge_{0.5}Si_{0.5}O_2$	11.730	3.416
$Ge_{0.5}Sn_{0.5}O_2$	19.415	3.527
$Sn_{0.5}Si_{0.5}O_2$	12.883	3.360

The lattice constant of the Si(0 0 1) surface is about 3.83 Å, therefore according to LDA results $Si_{0.5}Ge_{0.5}O_2$ is particularly favorable as it can be epitaxially grown on Si(1 0 0) without any strain. Using XO_2 and $X_{0.5}Y_{0.5}O_2$ for the generic notation of these i-phase crystals, we note that the O–X–O and O–Y–O bond angles are 109.47° and the X–O–X and X–O–Y bond angles are 180°. The elastic constants and dielectric permittivity tensor of each i-phase crystal are tabulated in Tables 2 and 3, respectively. The band structures for the compounds and ternary alloy crystals as obtained with KA pseudopotentials are displayed along the high-symmetry lines in Figs. 2 and 3 and the corresponding total DOS are shown in Figs. 4 and 5.

For all of the i-phase crystals under consideration the conduction band minima occur at the Γ point, whereas the valence band maxima are located at R point making them indirect band gap materials

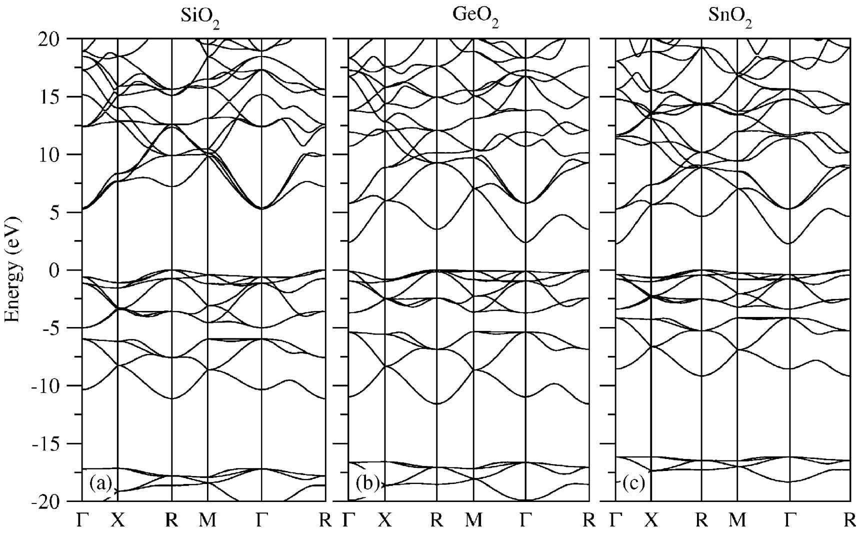

Fig. 2. LDA band structure of i-phase: (a) SiO_2; (b) GeO_2, and (c) SnO_2.

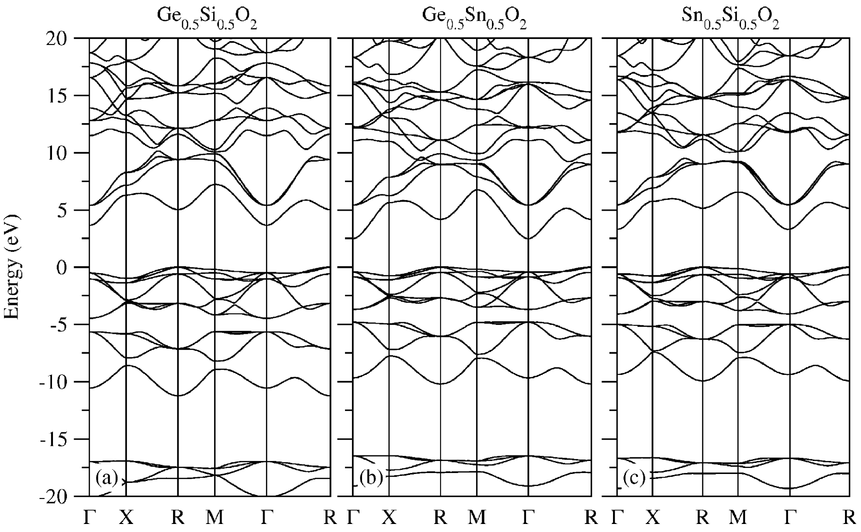

Fig. 3. LDA band structure of i-phase: (a) $Ge_{0.5}Si_{0.5}O_2$; (b) $Ge_{0.5}Sn_{0.5}O_2$, and (c) $Sn_{0.5}Si_{0.5}O_2$.

(cf. Table 4). However, the direct band gap values are only marginally above the indirect band gap values. A renown artifact of LDA for semiconductors and insulators is the underestimation of the true band gap values [3]. In this work we do not attempt any correction procedure to adjust the LDA band gap values. After these general comments, now we report the results of each lattice individually.

The simple cubic SiO_2 polymorph with the inverse Ag_2O structure (i-SiO_2) containing two molecules within the primitive cell has been very recently proposed by Ouyang and Ching [1]. The wide band gap, unusually high dielectric constant as in stishovite SiO_2 and the lattice constant compatibility to Si make this phase very attractive for electronic applications. We computed the electronic and structural properties of i-SiO_2 by using 65 Ha plane wave energy cutoff and 10 × 10 × 10 k-point sampling. The computed band structure and the total DOS of the i-SiO_2 shown in Fig. 2(a) and 4(a) are in good agreement with Ouyang and Ching [1]. Elastic constants and dielectric constants of the crystal are listed in Tables 2 and 3, respectively.

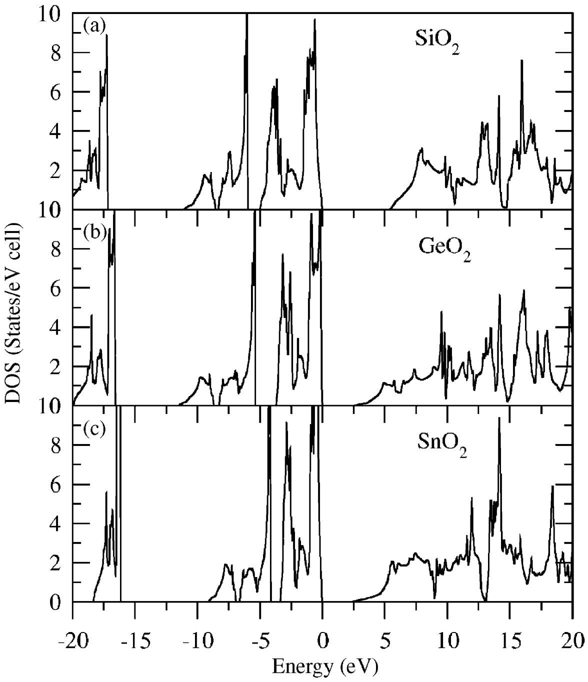

Fig. 4. Total DOS of i-phase: (a) SiO_2; (b) GeO_2, and (c) SnO_2.

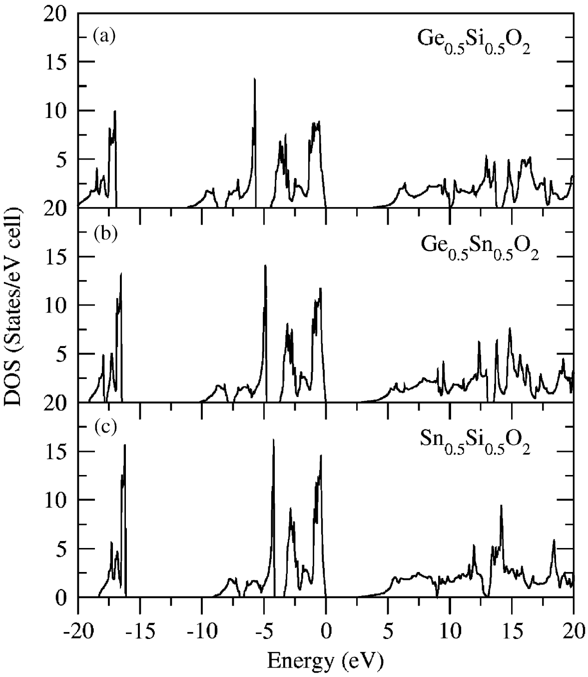

Fig. 5. Total DOS of i-phase: (a) $Ge_{0.5}Si_{0.5}O_2$; (b) $Ge_{0.5}Sn_{0.5}O_2$, and (c) $Sn_{0.5}Si_{0.5}O_2$.

Table 4
Indirect (E_g) and direct ($E_{g,\Gamma}$) LDA band gaps for each i-phase crystal

Crystal	VB Max.	CB Min.	E_g (eV)	$E_{g,\Gamma}$ (eV)
SiO_2	R	Γ	5.269	5.870
GeO_2	R	Γ	2.402	2.511
SnO_2	R	Γ	2.285	2.670
$Ge_{0.5}Si_{0.5}O_2$	R	Γ	3.666	4.179
$Ge_{0.5}Sn_{0.5}O_2$	R	Γ	2.487	2.900
$Sn_{0.5}Si_{0.5}O_2$	R	Γ	3.292	3.900

Motivated by the appealing features of i-SiO_2, we consider the electronic and structural properties of i-GeO_2, i-SnO_2 and their ternary alloys: $Ge_{0.5}Si_{0.5}O_2$, $Ge_{0.5}Sn_{0.5}O_2$ and $Sn_{0.5}Si_{0.5}O_2$. The plane wave energy cutoff and k-point sampling were chosen to get 0.001 eV energy convergence. The band structure and the DOS of i-phase crystals GeO_2 and SnO_2 can be seen in Figs. 2 and 4, respectively. An important concern is whether these cubic phases of SiO_2, GeO_2 and SnO_2 are stable or not. The requirement of mechanical stability in a cubic crystal leads to the following restrictions on the elastic constants: $C_{11} > C_{12}$, $C_{11} > 0$, $C_{44} > 0$, and $C_{11} + 2C_{12} > 0$. The elastic constants in Table 2 satisfy these stability conditions. Furthermore, we compute the phonon dispersion curves of these structures. It can be inferred from Fig. 6 that i-SiO_2 is at least locally stable whereas i-GeO_2 and i-SnO_2 contain negative phonon branches which signal an instability of these phases.

The band structures and the DOS of i-phase $Ge_{0.5}Si_{0.5}O_2$, $Ge_{0.5}Sn_{0.5}O_2$ and $Sn_{0.5}Si_{0.5}O_2$ are shown in Figs. 3 and 5, respectively. The ternary alloy elastic constants listed in Table 2 also satisfy the mechanical stability conditions. The computed phonon dispersion curves of these structures are locally stable as can be observed in Fig. 7.

4. Conclusions

Crystalline oxides can be considered as Si CMOS gate oxides if they can be lattice matched to Si, so that a high quality interface is obtained. In this respect, the i-phases of SiO_2, $Si_{0.5}Ge_{0.5}O_2$, $Si_{0.5}Sn_{0.5}O_2$ are particularly promising with their high dielectric constants besides their lattice match to Si, especially in the case of $Si_{0.5}Ge_{0.5}O_2$.

Furthermore, first-principles elastic constants, electronic band structures and phonon dispersion curves of these i-phase oxides have been obtained with high accuracy in this work. Given the phonon dispersion curves, GeO_2 and SnO_2 are predicted to

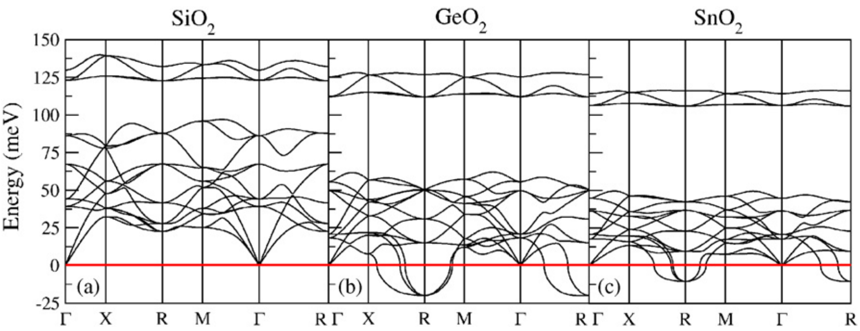

Fig. 6. Phonon dispersions of: (a) SiO_2; (b) GeO_2, and (c) SnO_2.

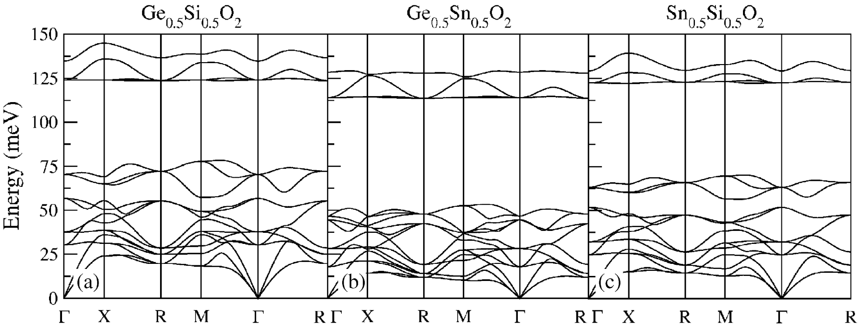

Fig. 7. Phonon dispersions of: (a) $Ge_{0.5}Si_{0.5}O_2$; (b) $Ge_{0.5}Sn_{0.5}O_2$, and (c) $Sn_{0.5}Si_{0.5}O_2$.

be unstable, while their alloys turn out to be stable within LDA; this needs to be tested with other approaches such as the generalized gradient approximation [3]. Finally, we note that we do not consider the thermodynamic stability of these i-phase oxides. Also, we should mention that for technological applications the epitaxial growth conditions become more critical as opposed to bulk system stability. A promising direction for further theoretical studies can be the finite temperature investigation of these i-phase isovalent structures on Si(1 0 0) surfaces using large number of monolayers.

Acknowledgments

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