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Full potential calculation of electronic properties of rutile RO_2 (R=Si, Ge, Sn and Pb) compounds via modified Becke Johnson potential

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ABSTRACT

The electronic properties of RO_2 (R=Si, Ge, Sn and Pb; a group IVA element) compounds in rutile structure have been calculated using WIEN2k implementation of full potential linearized augmented plane wave (FPLAPW) method. The exchange and correlation (XC) effects are taken into account by an orbital independent modified Becke Johnson (MBJ) potential as coupled with Local Density Approximation (LDA) for all the compounds except for PbO_2 where only Generalized Gradient Approximation (GGA) is considered for the same. We predict a direct band gap in all these compounds with continuous decrease as the atomic size of IVA element increases such that there is an appearance of semimetallic band structure for the last compound, PbO_2. The largest band gap (7.66 eV) has been found for SiO_2, which governs its insulating nature. We observe that MBJLDA results for band gaps of these compounds are far better than those obtained using GGA and Engel–Vosko's GGA (EV-GGA). A very good agreement is observed between MBJLDA band gaps with corresponding experimental values as compared to other calculations. The electronic band structures are also analyzed in terms of contributions from various electrons.

1. Introduction

Most of the IVA-based dioxide materials have high dielectric constant and wide band gap. These materials are of great interest to the research community due to their outstanding mechanical, chemical and high temperature properties. These compounds are also important from the geophysical point of view [1,2] and their electronic properties vary widely from insulating to metallic nature. Yamanaka et al. [2] prepared the single crystals of the rutile type polymorph of SiO_2, GeO_2 and SnO_2 and studied the bond character of these compounds using X-ray diffraction.

Among the RO_2 series, SiO_2 is one of the most common transparent materials in nature and its band gap is 8.9 eV [3], which is the largest among the known dioxides materials. Silica (SiO_2) based ceramics are good electrical and thermal insulators. These are used for alternative gate oxides and provide low-loss dielectric waveguides in the field of integrated optics [4,5]. From last decade, this wide band gap material has gained much interest due to its use in the nanocrystal devices [6]. There exist a number of experimental studies such as X-ray emission spectra, X-ray and ultraviolet photoelectron spectra (XPS and UPS), photoconductivity, optical reflectivity [7–14], etc., which reveal the detailed analysis of band structure and density of states (DOS) of SiO_2 with the prediction of large band gap in the DOS at the Fermi level (E_F). The XPS measurements [11] showed that the band gap in crystalline state of SiO_2 is larger than the amorphous state. On the other hand, the reflectivity spectra [13] of both states showed that the band structures are quite similar. Several theoretical efforts using Orthogonalized Linear Combination of Atomic Orbitals (OLCAO) method [15,16], simple Tight Binding method [17], Linearized Augmented Plane Wave (LAPW) method [18] and Plane Wave basis Pseudopotential method [1] were also made in order to calculate the energy bands at the symmetry points and total DOS of SiO_2.

GeO_2 (germania) has two stable polymorphs: α-quartz (hexagonal) and rutile (tetragonal) structures. The rutile structure is stable at ambient temperature and pressure whereas the quartz structure is stable above ~1300 K at ambient pressure [19]. Germania has chemical and structural properties similar to silica. Many experimentalists studied GeO_2 by X-ray diffraction, neutron scattering, spectroscopic techniques such as X-ray absorption spectroscopy (EXAFS/XANES), Raman spectroscopy, NMR spectroscopy and IR spectroscopy to find its phase stability by varying pressure [20–26]. On the other hand, several theoretical calculations to study the band structure [1,27,28], elastic properties [29], thermal expansion [30] and melting phenomenon [31] of germania also exist in literature.

On the other hand, SnO_2 (stannic oxide) is a very attractive semiconductor material, which finds great interest due to its

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outstanding electrical, optical and electrochemical properties. It also shows room temperature ferromagnetism (FM) after suitable doping with transition metal ions, which is an interesting property from spintronics point of view [32–34]. For these reasons, there are a large number of reports on electronic properties of SnO_2 both theoretically [32,35] and experimentally [3,36], which studied its band structure and DOS in details and found that it is direct and wide band gap semiconductor with a band gap at the center of the Brillouin Zone (BZ). Moreover, SnO_2 is also a key functional material in many applications such as transparent conducting electrodes, solar cells, gas sensors and in optoelectronic devices [35].

The last compound under investigation, PbO_2, has attracted considerable attention owing to its use as the active material for storage of chemical energy in lead acid batteries [37]. It exists in two structures: α-PbO_2 (orthorhombic—columbite structure) and β-PbO_2 (tetragonal—rutile structure) with space group Pbcn (V_h^{14}) and $P4_2/mnm$ (D_{4h}^{14}), respectively [37]. Under the normal conditions, β-PbO_2 is more stable structure [37]. The experimental studies of β-PbO_2 by photoemission spectroscopy, X-ray absorption and emission spectra [38] proved that conduction and valence band touched at E_F and after convolution with a broadening function, these appeared to merge. Therefore, this compound is best described as a semimetal. Payne et al. [38] studied the electronic structure of β-PbO_2 using Vienna ab-initio Simulation Package (VASP) within GGA formalism and predicted it as a semimetal. Robertson [39] calculated the electronic structures of rutile phase of SnO_2, GeO_2, PbO_2, TeO_2 and MgF_2 using the tight binding method and discussed the formation of band gap in terms of two center interactions: $P=p_\sigma$ (cation-p, anion-p) and $Q=sp$ (cation-s, anion-p).

Keeping in mind the change of physical state (insulator–semiconductor–semimetal) along the series RO_2 (R=Si, Ge, Sn and Pb), there is a strong reason to study the electronic properties of these compounds. Moreover, there is a finite mismatch between experimental and theoretical band gaps of most of these compounds. We have focused in this study on the trends observed in electronic properties by changing R atom along group IVA in present RO_2 compounds. To find the accurate band gap of present semiconductors, the band structures have been calculated using semilocal exchange-correlation potential (MBJLDA) such that MBJ exchange term is coupled with LDA correlation. These results have also been compared to those obtained from GGA, EV-GGA and with experiments to test the accuracy. There exist no other calculations for these compounds using MBJLDA and EV-GGA in the literature. The paper is organized as follows. Brief descriptions of MBJ potential and computational details are outlined in Section 2. The calculated results of electronic properties, band gaps and their comparison with available experimental findings are described in Section 3. Finally in Section 4, we summarize the results and draw a conclusion.

2. Theory and computational details

The modified Becke Johnson potential (MBJ) as proposed by Tran and Blaha [40] is

$$v_{x,\sigma}^{MBJ}(r)=cv_{x,\sigma}^{BR}(r)+(3c-2)\frac{1}{\pi}\sqrt{\frac{5}{12}}\sqrt{\frac{2t_\sigma(r)}{\rho_\sigma(r)}} \tag{1}$$

where $\rho_\sigma=\sum_{i=1}^{N_\sigma}|\psi_{i,\sigma}|^2$ is the electronic density, $t_\sigma=(1/2)\sum_{i=1}^{N_\sigma}\times\nabla\psi_{i,\sigma}^{*}\cdot\nabla\psi_{i,\sigma}$ is the kinetic energy density and

$$v_{x,\sigma}^{BR}(r)=-\frac{1}{b_\sigma(r)}\left(1-e^{-x_\sigma(r)}-\frac{1}{2}x_\sigma(r)e^{-x_\sigma(r)}\right) \tag{2}$$

is the Becke Roussel (BR) potential [41], which was proposed to model the Coulomb potential created by the exchange hole. x_σ is determined from an equation involving ρ_σ, $\nabla\rho_\sigma$, $\nabla^2\rho_\sigma$ and t_σ. Then b_σ is calculated by $b_\sigma=[x_\sigma^3e^{-x_\sigma}/(8\pi\rho_\sigma)]^{1/3}$. In Eq. (1), c is chosen such that it depends linearly on the square root of the average of $|\nabla\rho|/\rho$:

$$c=\alpha+\beta\left(\frac{1}{V_{cell}}\int_{cell}\frac{|\nabla\rho(r')|}{\rho(r')}d^3r'\right)^{1/2} \tag{3}$$

where α and β are the two free parameters, whose values are $\alpha=-0.012$ (dimensionless) and $\beta=1.023$ Bohr$^{1/2}$ and V_{cell} is the unit cell volume.

Due to the second term in Eq. (1), the Becke Johnson potential reproduces very well the step structure and derivative discontinuity of the exact exchange potential, which is an important result since only the semilocal quantities are used.

The RO_2 (R=Si, Ge, Sn and Pb) compounds crystallize in rutile structure, a structure with tetragonal ($P4_2/mnm$) symmetry [3,37] such that the unit cell contains two formula units (six atoms). In this structure, each R atom is coordinated by six oxygen atoms in an octahedral configuration whereas each oxygen atom is bounded by three R-atoms. In RO_2 compounds, the R atom is present at (0,0,0) and O atom is located at (u,u,0). The internal parameter u is 0.307 [42] for RO_2 (R=Si, Ge and Sn) and 0.310 for PbO_2 [43], which represents the relative displacement between R and O atoms. In order to compute desired calculations, we have employed the FPLAPW method, which is based on the density functional theory (DFT) [44] and is implemented in WIEN2k code [45]. The exchange and correlation (XC) effects were taken into account using the three approximations: GGA, EV-GGA [46] and MBJLDA [40]. The parameterization of Perdew–Burke–Ernzerhof (PBE) [47] has been used to construct the exchange-correlation potential for GGA formalism. The radius of MT sphere (R_{MT}) values for Si, Ge, Sn, Pb and O atom were taken to be 1.80, 2.0, 2.35, 2.45 and 1.50 a.u., respectively. The plane wave cut-off parameters were decided by $R_{MT}k_{max}=7$ (where k_{max} is the largest wave vector of the basis set) and $G_{max}=12$ a.u.$^{-1}$ for Fourier expansion of potential in the interstitial region. The **k**-space integration has been carried out using the modified tetrahedron method [48]. The self-consistency is obtained by 189 **k**-points in the irreducible Brillouin zone (IBZ) for all compounds.

3. Results and discussion

The semilocal exchange-correlation MBJLDA potential is valid for semiconductors and insulators mainly, i.e., for the solids with no overlap between occupied and unoccupied bands. As in these compounds, orbital independent MBJ potential could catch the essentials of orbital dependent potentials (or hybrid functionals such as the GW approximation) and thus predicts the band gaps of solids, which are in good agreement with experiments [49]. Due to the reported semimetallic nature of PbO_2, only GGA formalism has been used to predict its ground state properties. The electronic structure calculations of present RO_2 compounds have been performed at corresponding experimental lattice constants [2,43] as listed in Table 1. First of all, the total and partial density of states (DOS) of RO_2 (R=Si, Ge, Sn and Pb) compounds have been analyzed in the energy range from −10 eV to 10 eV as shown in Fig. 1. The total DOS increases in the vicinity of E_F with an increase in the size of R atom among present compounds. The valence band (VB) is filled up to E_F in all these compounds. The total DOS have qualitative similar characteristics in all but the band gap decreases continuously with the increase in atomic size of R atom. Ultimately, the band gap becomes negligible for the