Research Article

Basic Elastic Properties Predictions of Cubic Cerium Oxide Using First-Principles Methods

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Computational material methods were used to predict and investigate electrical and structural properties of cerium oxide (CeO_2). Density functional theory was used to obtain the optimized crystal structure and simulate the material's electronic and elastic responses. Oxygen to oxygen nearest neighbor distance is 2.628 Å, while oxygen to cerium distance is calculated to be 2.276 Å. The conduction band has a prominent set of bands, which exists between 6 and 17 eV. An indirect energy gap (6.04 eV) exists between the valence and conduction bands. The independent elastic constants allow a mechanical assessment on the suitability of cubic cerium oxide as a substrate for advanced electronic devices. The calculated results of phonon dispersion curves are also given.

1. Introduction

A significant need exists to develop materials not only capable of providing desired electronic properties but also capable of surviving at extreme temperatures during device fabrication, such as in cofiring. An excellent candidate material is the oxide-based ceramic ceria. Ceria with its cubic structure can provide a platform for the introduction of dopants that can alter its electrical properties from insulating to semiconducting through oxygen vacancies [1–4]. This oxide-based ceramic material also possesses the refractory nature needed for high-temperature operation. However, the proper selection of dopants has to this point been somewhat speculative in nature based upon empirical experimentation. With the use of computational methods, material properties can be evaluated and optimized before the material is processed allowing an optimized structure to be realized quickly. This saves enormous time and efforts of experimentally assessing properties of multiple changes in composition and structure. The purpose of this investigation is to predict electronic and static and dynamic lattice response of pure ceria.

2. Computational Methods

The commercial software package Material Studio, including the Cambridge Serial Total Energy Package CASTEP module was used to conduct these simulations [5]. The calculations were performed on a parallel computer cluster consisting of 14 AMD Opteron 64-bit processors utilizing a LINUX-based operating system. Starting with the base structure, a geometric optimization was performed to determine the initial lattice parameters and density. In this calculation, the generalized gradient approximation (GGA) [6] was used along with ultrasoft pseudopotentials to represent the atoms. Specifically, for this geometric optimization, the Perdew-Burke-Ernzerhof potential for solids (PBEsol) was used [7]. To obtain accurate band structures, calculations using the GGA PBEsol, as well as the hybrid functional Becke, three-parameter, Lee-Yang-Parr (B3LYP) potentials, were used [8, 9]. The finite element displacement method applied to a supercell of the geometrically optimized primitive lattice using norm-conserving potentials [10] to calculate the phonon dispersion curves was used. The real space cutoff radius was set to 5 Å which resulted in a supercell volume 27

FIGURE 1: Cerium oxide Fm-3m oxygen atoms denoted in red.

FIGURE 2: Electronic distribution in cubic ceria: band structure (a) and density of electron states (b).

times larger than the original unit cell. The quality of the q-factor spacing was set to $0.015 \text{ \AA}^{-1}$.

3. Results and Discussion

3.1. Crystal Structure. The ceria structure used for these calculations possesses the Fm-3m space group as seen in Figure 1. The geometric and electronic band structure calculations do not include thermal entropy effects. Therefore, these results are interpreted to occur at absolute zero temperature. The results of the calculation yielded a lattice parameter of $5.256 \text{ \AA}$ compared to their room temperature expected value

FIGURE 3: Distribution of the electrostatic potential in a vacuum between two (110) planes.

FIGURE 4: Phonon dispersion curves of cubic ceria.

of $5.410 \text{ \AA}$ [11]. The cerium to cerium distance is $3.717 \text{ \AA}$ while the next nearest neighbor cerium to cerium distance corresponds to the lattice parameter. The oxygen to oxygen nearest neighbor distance is $2.628 \text{ \AA}$ while oxygen to cerium distance was calculated to be $2.276 \text{ \AA}$. All lattice parameters remained orthogonal with the angles all being 90° . The total volume is $145.260 \text{ \AA}^3$ with an overall density of 7.870 g/cm^3 .

3.2. Electronic Properties. The starting electronic configurations are Ce $[\text{Xe}] 4f^1 5d^1 6s^2$ and O $[\text{He}] 2s^2 2p^4$. Figure 2 shows the band structure for a standard ceria unit cell. Three major band groups below the Fermi level are found centered at the following positions at -34 , -15 , and -2 eV , respectively, while other major band groups are located at 4 and 10 eV above the Fermi level. The indirect band gap in the G-X direction has a value of 6.04 eV which is in agreement with the experimental value [12]. The valence band begins at -5 to -1 eV and is dominated by the p orbital associated with the oxygen atoms. The lower band structures reveal large effective masses, due to the high radius of curvature of the bands, thereby prohibiting the promotion of carriers from below the Fermi level. The valence band consists of a spdf hybrid with dominant p character. In addition, the density of states for these bands is relatively small at 5 eV per volt. At levels below -10 eV the charges are bound, consisting of

FIGURE 5: Thermodynamic properties enthalpy, free energy, and entropy (a) and heat capacity (b).

hybridized d, s, and p orbitals. The conduction band has a prominent set of bands which exists between 6 and 17 eV. The highest valence band occurs in the GX direction with a value of 17 eV. An oxygen p orbital beyond the Fermi level, centered at 10 eV, forms the bond with the cerium pdf hybrid. The cerium atom contributes to the majority of the conduction band dominated by an f orbital and to a lesser degree p as well as d, which forms the oxygen bonds. However, the prominent f orbital above the Fermi level is reported to be unoccupied [13] but nonetheless forms a hybrid with some minor p and d character. The work function was determined by constructing dual two-dimensional arrays of the CeO₂ (110) surfaces separated by a vacuum gap of 30 Å. The electrostatic potential, determined midway of this gap, represents the energy required to remove one electron from the surface [14]. The (110) plane was selected as an intermediate between the (100) and (111) with regard to atomic population within a given plane. Figure 3 illustrates this potential profile between the two (110) planes in a vacuum. From this electrostatic potential versus fractional distance, the work function was calculated to be 5.287 eV.

3.3. Elastic Properties. The calculated elastic constants (C_{ij}) elements are given in (1). From the three independent elastic constants c_{11} , c_{12} , and c_{14} and bulk modulus ($B = 277.521 \pm 0.348$ (GPa)), the mechanical stability criteria of the cubic crystal may be evaluated using various symmetry-based relationships [15, 16]. For this case, c_{11} and c_{44} must be greater than zero as well as the respective quantities ($c_{11} - c_{12}$)

and ($c_{11} + 2c_{12}$). In addition, the bulk modulus must be greater than c_{12} but less than c_{11} , thus for ceria the mechanical stability requirements are met:

$$c_{ij} \text{ [GPa]} = \begin{bmatrix} 455.06 & 188.74 & 188.74 & 0.00 & 0.00 & 0.00 \\ 188.74 & 455.06 & 188.74 & 0.00 & 0.00 & 0.00 \\ 188.74 & 188.74 & 455.06 & 0.00 & 0.00 & 0.00 \\ 0.00 & 188.74 & 0.00 & 81.48 & 0.00 & 0.00 \\ 0.00 & 188.74 & 0.00 & 0.00 & 81.48 & 0.00 \\ 0.00 & 188.74 & 0.00 & 0.00 & 0.00 & 81.48 \end{bmatrix}. \quad (1)$$

For single-crystal ceria the predicted Young's modulus is 344.39 GPa along the three orthogonal axes. The polycrystalline bulk modulus was calculated as 277.52 GPa using the Voigt model which is comparable to the experimental value of 220 GPa [17]. The Poisson's ratio is 0.293, and the shear modulus was calculated to be 102.15 GPa. The elastic anisotropic factor ratio was calculated to be 0.773, which means polycrystalline ceria should be less susceptible to propagating microcracks at the grain boundary triple points [18], thereby facilitating its use as a suitable substrate for electronic devices.

3.4. Phonon Dispersion. The phonon is defined as the quantum of elastic strain energy. Therefore, the dispersion curves give insight into the material's thermal properties. For the cubic unit cell (N), the maximum number of branches, based

upon 3 atoms per cell (z), yields 9 degrees of freedom through the relationship $3Nz$ [19]. The relationship $(3z - 3)$ yields a maximum of six optical branches and hence the balance of three acoustic branches in any given direction. Figure 4 shows results of the phonon dispersion calculations. The lower acoustic branch in the G-X direction shows one acoustic longitudinal of higher energy than the transverse acoustic branch. The phonon dispersion curves become nondegenerate for all branches in the X-K direction giving the expected nine branches for this cubic structure. The higher frequency optical branches are split at the G symmetry point indicating some ionic bonding character [19]. The phonon dispersion calculation allows additional thermodynamic properties to be determined. The maximum Debye temperature was found to be 643 K. Figure 5(a) illustrates the enthalpy, free energy, and the temperature-scaled entropy as a function of temperature. The zero-point energy was found to be 0.178 eV. Figure 5(b) shows the temperature-dependent heat capacity per unit cell with a maximum value of 17 calories per Kelvin near the Debye temperature. The enthalpy was found to be -1914 eV.

4. Conclusions

It has been demonstrated that first-principles methods allow predictions of material properties and behavior of ceria. Judicious selection of a hybrid functional is necessary for the correct description of the electronic band structure for this insulating oxide-based material. Both static and dynamic lattice responses can be predicted, and the results can be used to guide processing and device fabrication. In future investigations, first-principles methods will be applied to obtain property predictions as a function of dopants and other processing variables.

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