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First-Principles Study of hydrogen retention and diffusion in beryllium oxide

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ABSTRACT

In the quest of new renewable sources of energy, hydrogen is a promising candidate and its storage in solid-state materials is of extreme importance. Beryllium has been invoked in the past for this purpose because of its low density, and for the rather low energy of adsorption and retention of hydrogen that makes its restitution relatively easy, therefore it seems interesting to also investigate the properties of beryllium oxide. Hydrogen (and its isotopes) is also important as the fuel of deuterium–tritium plasma in tokamaks for energy production by magnetically confined nuclear fusion, when the plasma is in interaction with the beryllium (and beryllium oxide) of the inner walls of the device.

Another interest of beryllium oxide (BeO) lies in its properties as a ceramic: high thermal conductivity, high electric resistivity, efficient accumulation of energy, and transparency to a large spectrum of radiations. The bad point is that beryllium oxide grows very easily as a film on pure beryllium sample and significantly perturbs the material properties on the surface in a manner that is not easy to comprehend.

The dynamics of hydrogen atom retention in beryllium oxide implies the knowledge of its interactions of the atoms constituting the material, on the surface and in the bulk and in the defects present into this media. These defects can be native or generated by the hydrogen beam. This paper proposes a detailed calculation of energy trapping and diffusivity of interstitial atoms (hydrogen, beryllium, oxygen). Then the same kind of computations is described for atomic vacancies and the trapping of hydrogen atoms into these vacancies. The last step deals with the surfaces of beryllium oxide, their structures and reactivity to hydrogen.

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1. Introduction

Beryllium oxide (BeO) is among the hardest known materials. It is the sole alkaline-earth oxide crystallizing in the hexagonal wurzite structure (polar group P63mc), a feature which can most probably be ascribed to the special electronic structure of beryllium and certainly bound to the fact that the Be – O chemical bond is not exclusively ionic but has also some covalent character. As a ceramic material, BeO possesses many precious properties such as exceptional hardness, high thermal conductivity, high electric resistivity, efficient accumulation of energy, and transparency to a large spectrum of radiations that make it very useful in many technologies. Nevertheless these properties can be dramatically affected by point defects, impurities as well as anionic and cationic atomic vacancies. In turn, impurities can combine with vacancies that could result in sharp alteration of the material properties. This kind of studies has been published already concerning pure beryllium ([1,2] and references therein) but very few on oxidized beryllium, only very recently an all-electron calculation was published on hydrogen storage in beryllium oxide clusters [3].

In the domain in renewable energy production, beryllium is a good candidate for hydrogen storage in fuel cells and internal combustion engines, as well as in energy conversion devices [4,5]. Regarding nuclear fusion technology [6], beryllium is planned for use as a plasma facing material; therefore hydrogen isotopes retention in this material is a major issue. In this function contrarily to many other ones, the very high oxidation potential of beryllium [7] is an advantage since it reduces the amount of impurities in the core plasma [8].

In these two potential applications the storage of hydrogen is realized in the bulk or on the surface by ion beam irradiation that provokes atom displacements, creating point defects, vacancies and interstitials.

The electronic structure of bulk BeO has been studied in pioneer works by Lichanot et al. [9,10] using periodic Hartree–Fock methodology without any electron correlation evaluation. An LDA study of electronic and optical properties of ten wurtzite crystals was published almost at the same time [11]. Sashin et al. contributed DFT and HF studies of the electronic band structure of BeO in comparison with MgO and CaO [12,13]. More recently a rather large series of papers was devoted to both the electronic structure of BeO and the influence of point defects

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on the electronic and magnetic properties of this oxide [14–18]. Recent publications have been dedicated to First-Principles studies of BeO and other alkaline earth oxide structures [19–22], but very few papers have dealt with the reactivity of the BeO bulk and of its surfaces [23,24].

This list is far from exhaustive, but it can be alleged that the reactivity of beryllium oxide is largely to be explored from the quantum point of view and more precisely the structure of the point defects, atomic vacancies, self interstitials and hydrogen atom impurities. Therefore the paper is organized as follows: the computational section provides details on the DFT method and the results it yields on the geometry and electronic structure of beryllium oxide. Section 3 relates to the reactivity of bulk BeO: dissolution and diffusion of interstitial atoms. Section 4 deals with anionic and cationic atomic vacancies, formation and diffusion energies, together with hydrogen atoms trapping. Section 5 addresses adsorption on beryllium oxide surfaces. Discussion and conclusions are proposed in Section 6.

2. Computational section

The calculations are performed within the framework of the spin-polarized gradient-corrected density functional theory (DFT) using the Perdew–Burke–Ernzerhof functionals (PBE [25]) and including a semi-empirical pairwise London damped dispersion correction (PBE-D2 [26]). A plane-wave basis set was used with an energy cutoff of 32 Ry (435 eV); the ionic core potential was modeled using Vanderbilt ultra-soft pseudopotentials. The oxygen pseudopotential was taken from the *Quantum-Espresso* library [27]. As for hydrogen and beryllium pseudopotentials, they were tested in detail in a previous paper [28]. Integration in the first Brillouin zone was performed using the 6 × 6 × 6 point Monkhorst–Pack sampling for bulk calculation and 6 × 6 × 1 for surfaces. The working supercell is the 3 × 3 × 2 multiple of the unit cell (72 atoms), it is the largest supercell whose **a** and **c** parameters are similar in magnitude and that makes the calculations feasible. For the model surfaces, we selected the largest practicable systems, the vacuum between two cells images in the **c**-direction is at least 10 Å, therefore when the adsorbing H is at 5 Å from the upper face, and it is also at 5 Å from the lower face of the translated slab, this distance proved largely in the past to ensure a zero interaction between the surface slab and the incoming adsorbate.

The formation energy of a defect X in charge state q is defined as [29,30]:

$$\Delta E^{f}\left[\mathrm{X}^{q}\right] = E_{\mathrm{tot}}\left[\mathrm{X}^{q}\right] - E_{\mathrm{tot}}[\mathrm{BeO}] - \sum_{i} n_i \mu_i + q[E_F + E_v + \Delta V] \qquad (1)$$

where $E_{\mathrm{tot}}[\mathrm{X}^q]$ is the total energy of super cell containing the defect, $E_{\mathrm{tot}}[\mathrm{BeO}]$ the total energy of the perfect crystal using the same super cell. n_{i} is the number of host atom ($n > 0$ for interstitial atom, $n < 0$ for vacancy creation) and μ_i is the chemical potential of element i, the last term is zero for a neutral defect. The chemical potential upper bonds [31] are defined such as in the extreme O-rich condition, $\mu_{\mathrm{O}} = \mu^0_{\mathrm{O}} = 1/2\ E_{\mathrm{tot}}[\mathrm{O_2}]$, the energy of an oxygen atom in the oxygen molecule. In Be-rich regime, $\mu_{\mathrm{Be}} = \mu^0_{\mathrm{Be}} = 1/2\ E_{\mathrm{tot}}[\mathrm{Be}]$, the energy of a beryllium atom in the pure metal (2 atoms per cell). The lower bonds are imposed by the relation $\mu_{\mathrm{Be}} + \mu_{\mathrm{O}} = E_{\mathrm{tot}}[\mathrm{BeO}]$, then the lower limit of $\mu_{\mathrm{O}} = \mu^{\mathrm{min}}_{\mathrm{O}} = E_{\mathrm{tot}}[\mathrm{BeO}] - \mu^0_{\mathrm{Be}}$. μ_{O} depends on experimental conditions and should be considered as a variable of the formalism.

The interaction energy of a hydrogen atom with the beryllium oxide bulk or defective is defined as:

$$\Delta E_{\mathrm{H}} \ = \ E_{\mathrm{tot}}[\mathrm{Be_mO_n} + \mathrm{H} – E_{\mathrm{tot}}\mathrm{Be_mO_n}] – \mu_{\mathrm{H}} \qquad (2)$$

where $E_{\mathrm{tot}}[\mathrm{Be_mO_n} + \mathrm{H}]$ represents the total system energy and $\mu_{\mathrm{H}} = 1/2\ E_{\mathrm{tot}}[\mathrm{H_2}]$ the energy of the hydrogen molecule calculated in the same unit cell.

The Helmholtz free energy, which is also the Gibbs free enthalpy of the system is:

$$G(T) = E^{\mathrm{el}} + E^{\mathrm{vib}} – TS^{\mathrm{vib}} + \mathrm{PV}. \qquad (3)$$

E^{el} is the DFT electronic contribution, E^{vib} and S^{vib} are vibrational contributions to the total energy and entropy, respectively; and T, P and V are temperature, pressure and volume. When the P and V variations are neglected and $T = 0$ K $G(0) = E^{\mathrm{el}} + E^{\mathrm{vib}}$ is known as the Zero Point Energy; hereafter, the energies given without any other specification must be understood as ZPE-corrected PBE-D2 free energies, no further temperature adjustment will be proposed.

The stationary state structures were optimized using the damped molecular dynamics algorithm implemented in the *Quantum-Espresso* package. All the atoms were included in the optimization procedure, without any geometry or symmetry constraint. The activation energies for trapping, detrapping and diffusion are evaluated using the Nudged Elastic Band (NEB) algorithm [32]. The NEB calculations are performed using sequentially 5, 7, and 9 and more images until convergence toward the activation energies. They provide the three PBE-D2 energies of the initial configuration (IS), of the transition state point (TS) and of the final state (FS). The ZPE correction is further added using Eq. (3), leading to the free enthalpies of these three systems.

Due to the large dimension of the working super-cell the phonon dispersions needed for evaluation of Eq. (3) are performed at the (0,0,0) point of the reciprocal crystal lattice within Density Functional Perturbation Theory [33], taking into account all degrees of freedom of the entire supercell when calculating trapping energies. The diffusive energies are corrected using only the diffusive atom modes with their coupling to the substrate's phonon modes.

The PBE-D2 calculated lattice parameters are $\mathbf{a} = 2.671$ Å and $\mathbf{c} = 4.341$ Å, in very good agreement with the experimental and theoretical values reported in [21] and in [34], respectively 2.699 and 4.385 Å. Considering that the goal is to describe the structure and reactivity of isolated defects, it is assumed here that these parameters are not perturbed by the defect generation and then the cell volume is constant.

It is well known that GGA density functionals yield poor results in band gap calculations; this problem has been largely discussed [29]. In the present case, the band gap, issued from the bands structure calculation is 8.0 eV (Fig. 1), smaller than the experimental band gap 10.6 eV [22] but in agreement with the other GGA calculations [11,35]. This error does not influence the formation energies of neutral defects, but may strongly affect those of charged defects. On the contrary the calculated valence bandwidth, 19.2 eV, is in excellent agreement with the experimental value 19.4 ± 0.3 eV [13].

The calculated density of states (DOS) displayed in Fig. 2a is very similar to that given by Ivanovskii et al. [17] in terms of general appearance. The projected DOS calculation also yields the Löwdin electron distribution analysis. It evidences the intra-beryllium transfer of electron: in total the beryllium atom generates 0.40 e^- on the 2s shell and 1.33 e^- on the 2p, which gives an effective total charge of $Q_{\mathrm{Be}} = 1.7352\ e^-$ (then the atomic net charge is $+0.26\ e^-$) for this atom in BeO and $Q_{\mathrm{O}} = 6.2135\ e^-$ (the charge defect is ascribable to the integration scheme imposed by the plane waves model). The Bader-Voronoi decomposition yields more ionic but not fundamentally different values of 1.4304 and 6.5695 e^-.

Of course the Löwdin as well as the Mulliken schemes have been extensively debated in many occasions and their results are purely indicative, nevertheless our results are very close to those of Xu et al. [11], 1.76 $e^-$for Be. It is worth noting that these values would advocate more for covalent than ionic material. Both series of values lead to the fractional ionic character (FIC [11]):

$$\mathrm{FIC} = |Q_{\mathrm{A}} \text{- } Q_{\mathrm{B}}|/(Q_{\mathrm{A}} + Q_{\mathrm{B}}) = 0.56. \qquad (4)$$

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