



Role of oxygen in materials properties of yttrium trihydride



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ABSTRACT

Numerous experiments have shown that the oxygen-free films of YH₃ possess the face-centered cubic (*fcc*) structure only at high pressures whereas oxygen-containing YH₃ films crystallize into the *fcc* lattice at ambient conditions. In this report, by means of first-principles simulations, we provide a detail understanding of the role of oxygen in stabilization of the *fcc* YH₃ under normal pressure. We performed the oxygen position preferences screening within the *fcc* unit cell along with geometrical optimization series and verified the major stability conditions. The main aggregate and electronic characteristics have been calculated in order to gain an insight into how the Y–O bond activation and coordination in the metallic matrix create new materials properties. The possibility of the compositional architecture on the base of *fcc* crystalline silicon and oxygen-containing YH₃ compounds has been suggested.

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1. Introduction

Oxygen containing YH₃ films exhibit a unique property of a light-induced change of their optical properties [1–4], which takes place at room temperatures under normal pressure. These novel hydride materials might present interest for several practical applications such as engineering of smart windows [2] and optoelectronic devices [5]. Analysis of experimental results reveals that the oxygen impurities play an important role in structural, electronic, and optical properties of the YH₃ films. For instance, from the time-resolved X-ray diffraction studies it was found [3] that the O-containing YH₃ films possess an insulating BiF₃-type structure with face-centered-cubic (*fcc*) lattice (referred to as YHO hereafter). Investigations of the optical properties showed that the electronic band gap (E_g) of the YHO films varies in a wide range [1,6].

At ambient conditions, the oxygen-free films of YH₃ crystallize in a hexagonal close-packed (*hcp*) structure. A *fcc* lattice becomes the energetically most favorable structure at the elevated pressure of about 8 GPa [7]. Studies of Machida et al. [8,9] demonstrated that at pressures of no less than 23 GPa, a *hcp*–*fcc* phase transition is accompanied with the electronic band gap closure. Detailed first-principles investigations of the O-free YH₃ compounds were carried out in a number of works (see, e.g., Refs. [10,11]). In contrast, neither the effect of chemical substitution nor structural and electronic properties have never been theoretically considered

for the recently developed ternary YHO materials. Evidently, the solid understanding of the processes governing stabilization and functioning of these compounds is of crucial importance for the further progress of experimental and technological work. Thus, the main goal of the present paper is to establish the physical mechanisms underlying the oxygen-induced stabilization of the *fcc* structure at ambient conditions as well as to give the proper description of principal features of the electron subsystem. In particular, we will address two fundamental issues, namely why just the oxygen atoms play the dominant role in suppression of lattice instability of the *fcc* phase of the O-free YH₃, and which new structural, mechanical and electronic properties are created by incorporation of a certain amount of oxygen atoms into the system of the metal host and hydrogen.

2. Structural model and computational details

Chemical background and selection of a model: Our theoretical efforts will be concentrated on the evolution of the YHO crystalline structure in terms of the oxygen content. From analysis of experimental data [3,6,12] one can summarize that (i) oxygen is incorporated into yttrium hydride films during a deposition process; simultaneously, there occurs some moderate deficiency of hydrogen atoms; (ii) oxygen demonstrates high reactivity with respect to yttrium; (iii) metal–insulator transition when the unstable metallic form of *fcc* YH₃ transfers into the semiconducting one takes place upon oxygenation process and is irreversible; (iv) the new phase corresponds to a stable solid with a similar *fcc* lattice structure; and (v) to date, none of the scientific reports have

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given any information concerning arrangements of O-impurities in the *fcc* lattice of YH_3 .

Taking now into account that hydration of a metal proceeds initially via hydrogen interstice positions, one can therefore suggest that uptake and fixation of oxygen in the yttrium lattice environment is the result of a competition between the diffusible oxygen and hydrogen atoms for the desired linking with yttrium atom. This effect appears in the process of interstitial dissolution and is caused by the robust chemical potential of yttrium, which, acting as a strong deoxidizer [13], tends to prevent O and H atoms from the chemical interaction with each other by binding one of them. Evidently, the irreversible incorporation of a noticeable amount of oxygen into the bulk of a Y–H system happens as a result of chemisorption and takes place inside the area enclosing a sufficient number of the dissociated oxygen and hydrogen atoms. This in turn permits a possibility of H→O substitution in the trapping process governed by the yttrium site. The ternary YHO compound formation can formally be represented in terms of the partial replacement by equation $\text{Y} + 3\text{H} + 2\text{xO} \rightarrow \text{YH}_{(3-2\text{x})}\text{O}_\text{x} + \text{x}(\text{H}_2 + \frac{1}{2}\text{O}_2)$, where the first term on the right side corresponds to the substitution and hydrogen off-stoichiometry effects, the second one relates to excess molecules, which are supposed to be evolved into environment. Two points should be noted in the context of the above reaction. First, the main benefit the oxygen has over the hydrogen for selectivity on binding with Y in the metallic matrix can be seen from comparison of the bond dissociation energies, namely 7.4 eV for the Y–O bond [14] and 3.5 eV for the Y–H bond [15]. Second, as oxygen is more

electronegative than hydrogen, an additional charge transfer along the new Y–O connection will give rise to a proper redistribution of the electronic density in the YHO system, which may provide an experimentally observed structural stabilization of a *fcc*-like phase of the oxygen doped YH_3 films.

Computational aspects: The periodic plane-wave-basis DFT simulations were carried out by using the Vienna Ab-initio Simulation Package (VASP) [16] together with the potential projector augmented-wave (PAW) method [17–19]. In the calculations the Perdew–Burke–Ernzerhof (PBE) [20] GGA exchange–correlation functional was utilized, the cutoff energy of the plane waves was set to 680 eV, and PAW pseudopotentials were adopted with $4s^2 4p^6 5^2 4d^1$, $1s^1$, and $2s^2 2p^4$ valence electron configurations for Y, H, and O atoms, respectively. A Γ -point centered mesh for the \mathbf{k} -point sampling was chosen as follows: $8 \times 8 \times 8$ for oxygen position preferences screening, geometry optimizations and stability evaluations; $16 \times 16 \times 16$ for electronic structure calculations. Theoretical modeling of an electronic structure was made at a force tolerance < 0.002 eV/Å and a convergence criterion of 1×10^{-8} eV. To narrow down the theoretical underestimation of the GGA band-gap, MetaGGA calculations with the TB-mBJ potential [21,22] were performed with the $12 \times 12 \times 12$ \mathbf{k} -point sampling. Graphic illustration of Fig. 1 was made using the VESTA program [23].

3. Results and discussion

Structural properties of the YHO system: In order to take into account the incorporation of oxygen via the H→O substitution and, correspondingly, to model the suppression of structural instability of the undoped *fcc* YH_3 , two hydrogen atoms occupied interstice positions of the original *fcc*-lattice were replaced by one oxygen atom. Such theoretical model corresponds to a chemical composition of $\text{YH}_{(3-2\text{x})}\text{O}_\text{x}$ with $\text{x}=0.25$, which is very close to an approximate composition of $\text{YH}_{2.4}\text{O}_{0.3}$ proposed in Ref. [3]. Next, screening of oxygen position preferences was carried out together with full geometrical optimization. The resulting choice for the oxygen position in the equilibrium lattice structure of the $\text{YH}_{2.5}\text{O}_{0.25}$ compound is presented in Fig. 1. Furthermore, note that its relaxed lattice parameter $a=5.233$ Å agrees well with the experimental value of $a=5.24$ Å [3].

The main structural feature of the unstable *fcc* form of YH_3 is that Y atoms occupy the sites of a face-centered cubic lattice, while hydrogens are distributed between two distinctive interstitial sites of the octahedral and tetrahedral types [24]. Our suggestion (examined in the present study) is that such arrangement of hydrogens is well chemically matched to allow their partial substitutions by the proper dopants that do not significantly affect the *fcc* lattice. As it follows from our DFT simulations, the

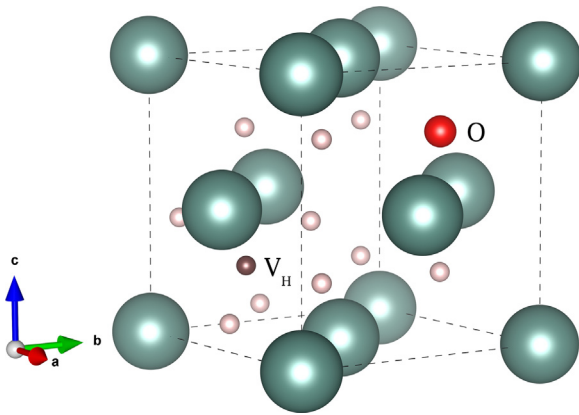


Fig. 1. (Color online) Schematic presentation of the *fcc* $\text{YH}_{2.5}\text{O}_{0.25}$ structure. The relaxed lattice constant $a=5.233$ Å. Y atoms are sketched by the large green color balls. The preferred oxygen position denoted by the red color ball corresponds to a slightly distorted tetrahedral site (0.7470, 0.7470, 0.7470) that is very close to the nominal site at $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$. The brown color ball depicts schematically the hydrogen V_H that was eliminated from the second tetrahedral position at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$.

Table 1

Frequency of low-lying zone center optical vibration Ω_0 (in cm^{-1}), and three linearly independent components of the elasticity tensor C_{ij} (in GPa) calculated for the $\text{YH}_{2.5}\text{O}_{0.25}$ structure. The macroscopic effective elastic parameters represented by the bulk (B), shear (G) and Young's (E) moduli (in GPa), and Poisson's ratio (ν) were estimated in terms of the Voigt–Reuss–Hill scheme [26]. In the last column the dimensionless Zener ratio [27] $Z = 2C_{44}/(C_{11} - C_{12})$ is indicated. For comparison, the elastic characteristics of cubic phase of single-crystal yttria Y_2O_3 and diamond cubic Si are quoted in the second and third rows, respectively. Mismatch degrees between the elastic characteristics of $\text{YH}_{2.5}\text{O}_{0.25}$ and *fcc* Si are shown in the last row.

	Ω_0	C_{11}	C_{12}	C_{44}	B	G	E	ν	Z
$\text{YH}_{2.5}\text{O}_{0.25}$	154	166.7	62.2	85.8	97.0	70.3	169.9	0.21	1.64
Y_2O_3 :									
Ref. [28]					135.7	66.5	171.5	0.30	
Ref. [29]		223.7	112.4	74.6	149.5 (± 1.0)	66.3 (± 0.8)	173.0 (± 2.0)	0.31	1.34
Ref. [30]					148.9 (± 3.0)	69.2 (± 2.0)	179.8 (± 4.8)	0.30	
<i>fcc</i> Si:									
Ref. [31]		165.6	63.9	79.5	97.8	66.5	162.5	0.22	1.56
Mismatch with respect to <i>fcc</i> Si		0.66%	2.66%	7.92%	0.82%	5.71%	4.55%		

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