

SECTION 1. SMART MATERIALS, COMPUTER MODELLING, ICT AND SUSTAINABILITY

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DEVELOPMENT OF YO AND YOH MODELS FOR AB INITIO CALCULATIONS

A. Gopejenko^{*1}, A. Gruodis, J. Purans¹, D. Bocharovs¹, S. Piskunov¹

¹*Latvijas Universitātes Cietvielu fizikas institūts, Rīga, LV-1063, Latvia*

²*Institute of Chemical Physics, Vilnius University, Vilnius, 10257, Lithuania*

**Corresponding author's e-mail: agopejen@inbox.lv*

Abstract

The fundamental research project aims to develop accurate first-principles models for yttrium oxide (YO) and yttrium oxyhydride (YHO), essential rare earth materials with promising applications in spintronics, superconductivity, and smart windows. In this study, *ab initio* have been performed using CRYSTAL23 computer code to investigate the structural and electronic properties of YO and YOH. A NaCl-type cubic structure was employed as the base model for YO, and hydrogen atoms have been systematically introduced into tetrahedral interstitial sites to simulate YOH with a hydrogen concentration up to 33.33%. The lattice parameter of YO was calculated to be 4.78 Å, in good agreement with previous theoretical data, and increased to 5.61 Å with the increase of hydrogen concentration. Density of States (DOS) analyses reveal that YO exhibits metallic characteristics with oxygen-dominated valence bands and yttrium-dominated conduction bands, whereas YOH displays semiconducting behaviour with a band gap of 3.13 eV and contributions to the valence band primarily from oxygen and hydrogen.

Key words: density functional theory, yttrium oxide, yttrium oxyhydride, smart windows

1 Introduction

Rare earth oxides (REO) are important for a wide range of applications such as superconductors, lasers, thermal barrier coatings, ceramics, etc. [1]. The increase in demand in REO is expected due to their use in technologies such as magnets, aircraft engines, optical devices as well as green and renewable energy technologies such as wind turbines, electric and hybrid

vehicles. REO are used in the strongest magnets, e.g. NdO is used in hard drives and loudspeakers. CeO is used as a catalyst in fuel cells. REO are widely used for the glass manufacturing with special optical properties necessary for camera lenses, telescopes, glasses.

Density functional theory (DFT) and lattice dynamics calculations predicted and characterized YO formation and energetics. The insights gained from these calculations allowed to successfully synthesise pure YO at 15 GPa and 1600°C [1]. However, it was found that YO is both thermodynamically and kinetically metastable and rapidly decomposes on heating. YO epitaxial thin film has been recently synthesized by pulsed laser deposition method [4].

RE metal oxy-hydrides (REHO) and, in particular, yttrium oxy-hydride (YOH) thin films are a novel class of mixed-anion inorganic materials known for their photochromic effect and light-induced resistivity change at room temperature and ambient pressure [2,3]. These switchable optical and electrical properties make them suitable for various technological applications, including energy-saving smart windows [4], sensors, ophthalmic lenses, and medical devices. However, to fully utilize YOH materials in these applications, a deep understanding of their structural properties and their dependence on physical properties is required.

YO model (Figure 1) has been created based on NaCl-type structure, which is typical for RE monoxides.

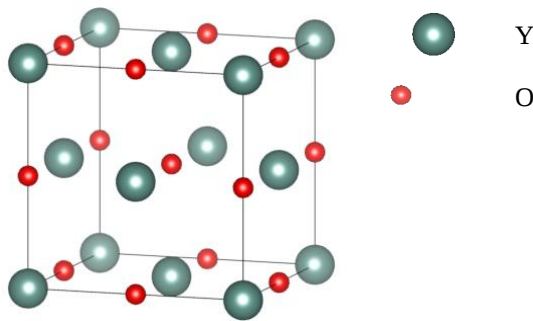


Figure 1. YO model used in the calculation

Within the framework of this study *ab initio* calculations of YO have been performed using CRYSTAL23 computer code [5,6], which allowed to determine the lattice constants, stability of the system under investigation. H atoms have been added to tetrahedral interstitial positions increasing H concentration from 0% (YO) to 33.33% (YOH).

DOS plots have been constructed for all calculated configurations. The comparison of DOS plots has been performed.

2 Computational details

CRYSTAL23 computer code [5,6], which employs Gaussian-type functions centred on atomic nuclei as the basis sets (BS) for an expansion of the crystalline orbitals has been used to perform hybrid DFT calculations. The following BSs have been used in the calculations: Y – Y_POB_TZVP_rev2, O – O_pob_TZVP_rev2, and H_pob_TZVP_rev2.

Heyd-Scuseria-Ernzerhof hybrid exchange–correlation functional (HSE06) [6], which uses a screened hybrid functional and includes the exact nonlocal Fock exchange has been used in the calculations.

To perform the modelling of the defects supercells with the extensions of $2 \times 2 \times 2$ have been created.. The Brillouin zone has been sampled by $8 \times 8 \times 8$ Pack-Monkhorst net [7].

3 Results

The calculated lattice parameters for both bulk and supercell of Fm-3m YO are $a_0 = 4.78 \text{ \AA}$, which is in a good agreement with the lattice constant of $4.87 \text{ \AA}$ reported in ref. [1].

Increase of H concentration resulted in the increase of the lattice constant to $5.61 \text{ \AA}$ for YOH configuration. The position of H atoms in the lattice resulted in a noticeable distortion of the crystal lattice for some of the configurations.

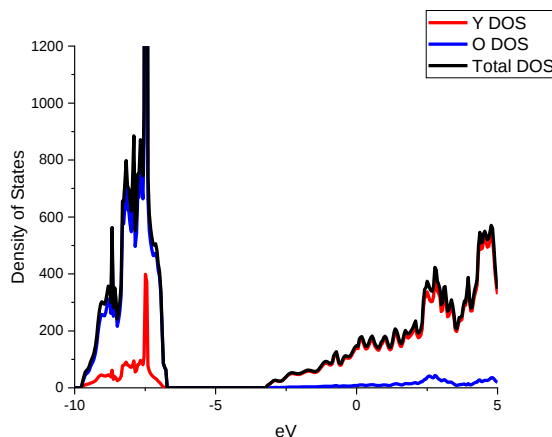


Figure 2. Projected DOS for YO

Figure 2 shows projected DOS plot for YO. DOS plot shows that O atoms are the primary contributors to the valence band, while Y atoms also contribute, but to a lesser extent. Y atoms are main contributors to the conduction band, while O atom contribution to the conduction band is minimal.

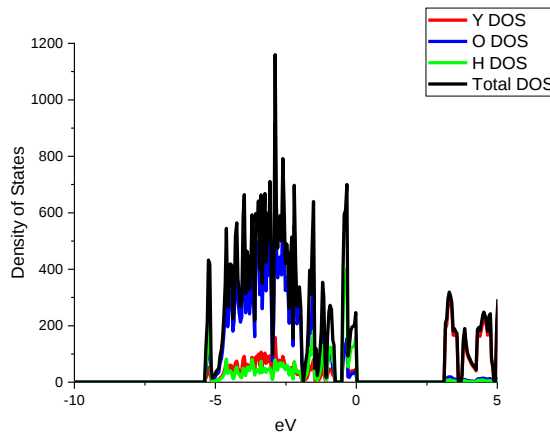


Figure 3. Projected DOS for YOH

Figure 3 shows projected DOS for YOH. The analysis of the calculations revealed that YOH is a semi-conductor with the assessed band gap of 3.13eV. O and H atoms are primary contributors to the valence band, while Y atom is primary contributor to the conduction band.

4 Conclusions

Calculations YO have been performed using the Crystal computer code. The calculated lattice parameters are in a good agreement with other theoretical studies.

Adding defect atoms significantly affect both atomic and electronic properties of the materials. DOS have been constructed and analysed for the calculated configurations.

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References

- [1] B. L. Brugman, Y. Han, L. J. Leinbach, K. Leinenweber, A. van de Walle, S. V. Ushakov, Q-J Hong, and A. Navrotsky, *Chem. Mater.* 2024, 36, 1, 332–339
- [2] T. Mongstad, C. Platzer-Bjorkman, J.P. Maehlen, L.P.A. Mooij, Y. Pivak, B. Dam, E.S. Marstein, B.C. Hauback, S.Zh. Karazhanov, *Solar Energy Materials and Solar Cells* 95 (12), (2011), 3596-3599
- [3] F. Nafezarefi, H. Schreuders, B. Dam, S. Cornelius, Photochromism of rare-earth metal-oxy-hydrides, *Appl. Phys. Lett.* 111 (2017) 103903.<http://www.crystal.unito.it/>.
- [4] S.S. Kanu, R. Binions, Thin films for solar control applications, *Proceedings of the Royal Society A* 466 (2010) 19–44
- [5] R. Dovesi, F. Pascale, B. Civalleri, K. Doll, N.M. Harrison, I. Bush, P. D'Arco, Y. Noël, M. Rérat, P. Carbonnière, M. Causà, S. Salustro, V. Lacivita, B. Kirtman, A. M. Ferrari, F.S. Gentile, J. Baima, M. Ferrero, R. Demichelis, M. De La Pierre, The CRYSTAL code, 1976–2020 and beyond, a long story, *J. Chem. Phys.* 152 (20) (2020) 204111, <https://doi.org/10.1063/5.0004892>.
- [6] J. Heyd, G.E. Scuseria, M. Ernzerhof, Erratum: “Hybrid functionals based on a screened Coulomb potential” [*J. Chem. Phys.* 118, 8207 (2003)], *J. Chem. Phys.* 124 (21) (2006) 219906, <https://doi.org/10.1063/1.2204597>
- [7] H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations, *Phys.Rev. B* 13 (1976) 5188–5192