SECTION 1. NANO TECHNOLOGIES, COMPUTER MODELLING

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DEVELOPMENT OF THE MODEL FOR YTTRIUM MONOXIDE *AB INITIO* CALCULATIONS

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Abstract

Rare earth oxides and monoxides are important for a wide range of applications. A model for the calculations of yttrium monoxide has been developed within the framework of this study. This model has been applied for the *ab initio* calculations of perfect YO to test whether it reproduces the basic parameters of the materials. Then the calculations varying the concentration of Y and O vacancies as well as with the addition of H atoms have been performed to assess the influence of these defects on atomic and electronic structure of the materials. The calculation revealed noticeable relaxation around the defect atoms in the calculated models as well as defects induced significant changes in the electronic structure of YO.

Key words: *density functional theory, ab initio calculations, yttrium monoxide.*

1. Introduction

Rare earth (RE) oxides are have an important role in a wide range of application, e.g. as superconductors, lasers, thermal barrier coatings, ceramics etc. Usually RE oxides are wide bandgap insulators such as Y_2O_3. Y_2O_3 is one of the most stables oxides and it possesses a closed shell trivalent RE ions. The most common valence for yttrium is +3, however, it is also capable of forming compounds, where it has an oxidation state of +2. Yttrium is able to exhibit different oxidation states due to its electronic configuration and its position in the periodic table as a transition metal [1].

RE monoxides are of interest for spintronics applications and might also be useful as conductors and ferromagnetic semiconductors. E.g., YO is a tuneable semiconductor at ambient conditions while LaO is superconducting.

There studies of YO are scarce. YO phase diagram studies by applying *ab initio* methods have been performed in ref. [2]. The results of the modelling determined a metastable structure of YO, which has been attributed to the resistive switching between Y_2O_3 and YO due to the similar stoichiometry of Y_2O_3 parent oxide. Orthorhombic Pnma-YO might be considered as oxygen deficient cubic Y_2O_3, while P4/nmm is pseudo-degenerate to the orthorhombic Pnma-YO. Phase stability calculations of the Y-O systems performed in ref. [3] determined that under pressure several Y-O compounds including YO become thermodynamically stable. NaCl-type structure of YO with Fm-3m symmetry was found to be stable at 9.9 GPa, while Pnma and P4/nmm were found to be thermodynamically unstable in relation to Y_2O_3 with additional Y atoms.

Within the framework of this study ab initio calculations of YO have been performed using Crystal computer code, which allowed to determine the lattice constants, stability of the system under investigation. Y and O vacancies have been calculated as well as the effect of vacancies on the structure. DOS have been constructed for both ideal YO and YO containing both Y and O vacancies. The comparison and analysis of DOS plots have been performed and analysed.

2. Computational details

CRYSTAL17 computer code [4,5], 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 2×2×2 have been created. The supercells contained 16, 64, and 32 atoms for Fm-3m, Pnma and P4/nmm structures, respectively. The Brillouin zone has been sampled by 8×8×8 Pack-Monkhorst net [7] with 29, 260, and 75 k-points for Fm-3m, Pnma and P4/nmm structures, correspondingly. For the calculations of YO under external pressure parameter EXTPRESS has been used in the input.

3. Results

The calculated lattice parameters for both bulk and supercell of Fm-3m YO are a0 = 4.78 Å.

The calculations of YO have been performed at normal pressure, 10GPA, 20GPA, and 30GPA pressures. The lattice parameters in YO have decreased to 4.70Å under 10 GPA pressure, 4.63Å under 20 GPA pressure,

and to 4.58Å under 30 GPA pressure. The compression of YO lattice was also accompanied by a reduction of the effective charge of yttrium atoms.

Introduction of the O vacancy resulted in a slight increase of the lattice parameter to 4.79 Å, while introduction of two O vacancies leads to a noticeable increase of the lattice parameter along the defect axis.

Comparing to O vacancies introduction of Y vacancy resulted in a noticeable decrease of the lattice parameter to 4.75Å. Two Y vacancies lead to a larger distortion of the supercell compared with two O vacancies along the defect axis.

H defect atom calculations have been performed by placing H atom in tetrahedral positions or octahedral position replacing O atom. Substitution of O atom by H atom resulted in slight increase of the lattice parameters to 4.80 Å, while adding H atom to the tetrahedral position resulted in a larger increase of the lattice parameters to 4.82Å. Adding two H atoms to the tetrahedral positions resulted in a significant increase of the lattice parameters to 4.98Å. Positioning of H atom in the tetrahedral and closest octahedral sites resulted in the increase of the lattice parameter to 4.82Å.

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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