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Structural stability, electronic and thermodynamic properties of $VOPO_4$ polymorphs from DFT+U calculations

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ABSTRACT

$VOPO_4$ compounds are rich in polymorphs and have important applications in catalysis and as electronic functional materials. Tetragonal α1-, monoclinic α1, α2, and β polymorphs of $VOPO_4$ have been investigated by using first principles calculations within density functional theory (DFT) improved by on-site Coulomb interactions (DFT+U) to better understand their thermodynamic and electronic properties. Structural and electronic properties, as well as relative stabilities for the four polymorphs, were calculated using DFT+U with both GGA and LDA exchange and correlation functionals. The effect of Hubbard U value was evaluated systematically and it is found that, although the relative stability of some polymorphs is not sensitive to the choice of U values, the relative stabilities between monoclinic α1 and α2 phases varied significantly with the choice of U values. The electronic density of states (EDOS) also changed with U values; the band gap first increased and then, when higher than 6, extra states were observed in the conduction band in some of the polymorphs, and the result was a band gap decrease. Clearly, an optimal U value in the range of 6–6.8 is desired for DFT+U calculations of $VOPO_4$ polymorphs. Investigating the effect of change of U value on thermodynamic stability and electronic band gap behaviors can thus be a criterion to decide optimal U values for further calculations such as surface adsorption and surface reactions of these compounds.

1. Introduction

Their outstanding catalytic and electronic properties make Vanadium phosphates ($VOPO_4$) structures an oxide functional material that is of great interest. For example, $VOPO_4$ have been investigated widely as catalysts for partial oxidation of hydrocarbons [1–4], in which the V^{5+} is important to abstracting H-atom from alkanes [5,6]. In addition, $VOPO_4$ compounds are promising cathode materials for lithium ion secondary batteries where lithium intercalation can happen in the layered structures, and operating potential can reach 4 V [7,8]. Density Functional Theory (DFT) has been used extensively to study atomic and electronic structure [9], thermodynamic properties [10], and chemical reaction mechanisms of transition metal oxides [11]. DFT calculations have also been used to supplement experimental investigations in identifying metastable phases and optimal reaction routes [12].

Conventional density functional theory (DFT) methods are well-known to overestimate electron delocalization and to underestimate the band gap of metal oxides. These issues become more severe for transition or rare earth metals oxides that contain *d*- or *f*-valence electrons [13,14]. To better predict the behavior of $VOPO_4$, the DFT+U [15,16] approach has been used commonly to provide a more accurate description of electron localization and band gap behaviors. The essence of the DFT+U method is that the introduction of a Hamiltonian term based on the Hubbard model [17] to describe the total energy for systems with both Coulomb repulsion and exchange interaction can prevent additional delocalization of *d*- or *f*-electrons [18]. This approach has proved successful when applied on systems such as TiO_2 [18], CeO_2 [19], and MgO [20], in which structural and electronic properties predicted by traditional DFT failed to agree with experimental results Vanadium oxides such as V_2O_5 [21] and VO_2 [22] have also undergone extensive theoretical investigations with the DFT+U method.

Despite the success of the DFT+U method in calculations of transition metal oxides, the choice of the U value is largely empirical. Usually, the U value is determined empirically by fitting it to specific experimentally determined physical properties, in which lattice parameters and band gap are most commonly used [23–25]. However, with the DFT+U approach, it is commonly observed that no single U value can reproduce all the properties; therefore, the choice of U is to minimize the average error in several

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properties [26]. DFT+U method is important not only for bulk structures and properties, but also for future surface adsorption and reaction energetic studies. Therefore, how to determine the correct U value for DFT calculations poses as a challenge in metal oxide calculations. In particular, very few studies have performed on $VOPO_4$ polymorphs, despite their potential applications as a functional material, within DFT+U calculations. The multiple polymorphs of $VOPO_4$ and the lack of data of some of the polymorphs have further complicated the choice of the U value. The main goal of this paper is to determine the proper U value for the $VOPO_4$ system, thereby to enable calculations of other possible physical properties and chemical interactions.

Vanadium phosphates exhibit many polymorphs under experimental conditions at different pressures and temperatures, and these polymorphs exhibit varied catalytical and electrochemical properties [27]. There are seven reported $VOPO_4$ polymorphs: tetragonal α1, α2, δ, and ω, orthorhombic β and γ, and monoclinic ε [28]. In addition, Gautier et al. reported a monoclinic α1 model obtained by layer translations in the tetragonal α1 polymorph, and confirmed it by using X-ray powder diffraction and a refinement through the DIFFaX+ [29]. Due to similar experimental synthesis conditions for most $VOPO_4$ polymorphs, obtaining the pure phase is a significant challenge and thus difficult to characterize experimentally [28]. Therefore, atomistic computer simulation is a useful method to investigate the properties of $VOPO_4$ polymorphs.

Typically, all structures of $VOPO_4$ polymorphs consist of VO_6 octahedron and PO_4 tetrahedron. The VO_6 octahedron is so strongly distorted that it is often considered a VO_5 pyramid with a short V═O bond on top and a long V···O bond on the bottom [30], as demonstrated in Fig. 1. The distorted VO_6 octahedron shares common vertices to form infinite O═V···O chains. PO_4 groups form bridges between these chains, and result in 3D frameworks.

Four polymorphs of $VOPO_4$, tetragonal α1 (mentioned as α1-tetra), monoclinic α1 (mentioned as α1-mono), α2, and β phases were studied in the present research. Fig. 1 demonstrates the schematic structures of these polymorphs as well as the distorted VO_6 and PO_4 polyhedron. α1-tetra, α1-mono, and α2 $VOPO_4$ polymorphs exhibit clear layered structures, with V···O connecting two successive layers [31]; while for β-$VOPO_4$, the tilting VO_6 octahedra result in zig-zag O═V···O chains, with PO_4 tetrahedra connecting the adjacent layers [32]. Comparing with binary Vanadium oxides, the $VOPO_4$ oxides have received much less attention, especially on simulation. Very little simulation work on $VOPO_4$ system is in the literature. Chen et al. [33] reported phase stability and electrochemical properties of $VOPO_4$ polymorphs by using the DFT+U method. Meanwhile, Gautier et al. [29] studied layered α1 and α2 $VOPO_4$, and they reported a new monoclinic form of α1 phase.

The present work provides a DFT+U study on the structures, relative phase stability of α1-tetra, α1-mono, α2, and β $VOPO_4$ polymorphs over a broad range of U values (0–8); and discusses a detailed investigation of the effect of the choice of U on electronic and structural behavior of α1-mono and α2 polymorphs.

2. Computational methods

Density Functional Theory (DFT) calculation used in this work was carried out by using the Vienna *ab initio* simulation package (VASP) [34]. Calculations were performed within the generalized gradient approximation (GGA), using the PBE [35] parameterization; and the local density approximation (LDA) with the CA [36] parameterization. The projection augmented wave (PAW) pseudo potential was used to describe the core electrons. The LDA and GGA exchange-correlation functionals have been used together with LDA+U and GGA+U in VASP. The simplified rotationally invariant form proposed by Dudarev [37] was introduced in our DFT+U calculations. Within the approach, the on-site coulomb term U and the exchange term J can be grouped together into a single effective parameter (U–J), and this effective parameter will be referred to simply as U. Effective U values of U = 2, 3, 4, 6, 8, and 10 eV were used for the V-*3d* and Zn-*3d* states. Electronic wave functions are expanded in a plane wave up to a kinetic energy cut-off of 400 eV. The first Brillouin zone was sampled using a $3 \times 4 \times 4$, $4 \times 4 \times 5$, $3 \times 3 \times 5$, and $4 \times 4 \times 4$ Monkhorst-Pack k-point mesh for α1-mono, α1-tetra, α2, and β $VOPO_4$ polymorphs calculations, respectively.

The four different structures considered in this study are shown in Fig. 1. The equation of states of the each of the polymorphs were calculated by performing calculations at various constant volumes with volume ranging plus and minus 10% of the experimental value. The total energy versus volume curve was, then fitted to the Birch equation of state [38], from where equilibrium volume and energy were obtained. Enthalpy as function of pressure curves were also calculated based on the energy volume curves, by using the total internal energy supplemented by the standard PV term [39].

3. Results

3.1. Structure relaxations and phase stability

Equilibrium lattice parameters and related properties for the four polymorphs of $VOPO_4$ were calculated within GGA+U and LDA+U with U = 2, 3, 4, 6, and 8. Calculated equilibrium lattice parameters for $VOPO_4$ polymorphs compared with experimental values [29,40,41] are concluded in Tables 1 and 2. Generally, all unit cell volumes are overestimated within the GGA method and are underestimated within the LDA method. Tables 1 and 2 show that overestimation increases with increased U value within the GGA+U, while underestimation within the LDA+U decreases with the growing of U. This result indicates that increased U value leads to expansion of the volumes for all $VOPO_4$ polymorphs. A similar phenomenon was observed in TiO_2 and Cr_2O_3. Ma et al. reported that the relation between lattice volume and applied U value depended greatly on the occupation of *d* orbital in metal oxides [42]; for those metal oxides with a full occupied *d* orbital (*d* electrons = 10), the lattice volume will decrease as U value increases. On the other hand, cell volume will increase as U value increases when U is applied to metal oxides with half-filled *d* orbital (*d* electrons <10), just as our case demonstrates.

To further investigate the effect of U value on volume, the volume difference ratio as a function of U value with respect to conventional GGA/LDA approaches was calculated. Fig. 2 demonstrates the variation of the volume difference ratio for the four polymorphs. The percentage number indicates the range of a volume increase under the impact of a U value. Note that the results from the LDA method have a lower impact on α1-tetra and α2 phases than using GGA. Deviations of volumes are 1.58% for α1-tetra using GGA and down to 0.72% using LDA, with U value of 8. For α2 phase, within GGA+U and LDA+U, volumes increase by 1.23% and 0.84% with a U value of 8, respectively; while for α1-mono and β phases, the LDA and GGA methods predicted similar amounts of volume increase. In addition, α1-mono and α1-tetra exhibit deviations larger to the α2 phase within GGA+U; while for the β phase, volume increases by 0.96% at U value of 6 and boosts to 1.79% with U value of 8.

Despite the lack of experimentally deducted band gap values for some polymorphs in the $VOPO_4$ system, the relative stability among polymorphs, which also was affected by the value of U,