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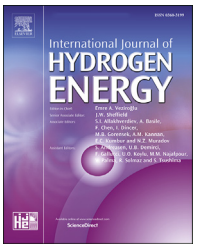

Short Communication

First-principles screening visible-light active delafossite ABO_2 structures for photocatalytic application

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ABSTRACT

Delafossite structures with composition ABO_2 have attracted great attention for various applications owing to their adjustable electric and optical properties. However, the photocatalytic usage of ABO_2 materials is still limited, owing to the various composition of chemical elements which makes it hard to be studied and fabricated. In this work, the stabilities, electronic, and optical properties of 40 kinds of Ag and Cu based delafossite ABO_2 materials have been investigated to tap the potential of photocatalytic applications by performing first-principle calculations. The bulk structure of ABO_2 are derived by minimizing the total energy. The electronic properties have been studied through the calculations of band structure, density of states (DOS), and work functions by using the method of GGA + *U*. The calculated results indicate that 4 kinds of them has superior stability, as well as appropriate electronic and optical properties for photocatalytic applications. Among them $Cu_3Zn_2TaO_6$ has the highest visible light absorption coefficient, indicating its immense potential for photocatalytic applications. This work presented some based physical properties of Ag and Cu based ABO_2 structures, and will promote the applications of ABO_2 materials.

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Introduction

Since the discovery of artificial photosynthesis [1], numerous researchers have attempted to promote the energy efficiency of hydrogen production from water splitting [2–5]. Meanwhile, delafossite ABO_2 materials often exhibit p type behaviors, and are widely used in various fields, such as transparent electrodes, solar cells, thermoelectric materials and photovoltaics applications [6–13]. Therefore, they attracted worldwide attention, especially Ag and Cu based ABO_2 materials [14–16].

Generally, delafossite ABO_2 materials belong to the space group of $R\bar{3}m$ and have the hexagonal structure, which can be viewed as a layer structure with the sequence A-O-B-O-A along the c-axis [14]. The delafossite structure has two cation sites (A^{+1} and B^{+3}) and one anion site (O^{-2}), which makes it electrically conductive due to its hole coming from of the vacancy of A^{+} and O^{2-} located in the interstitial void [17,18]. A considerable amount of experimental [19–23] and theoretical [24–28] study has been reported in the investigation of ABO_2. Saadi S discovered that $CuCrO_2$ can produce hydrogen when S^{2-} is used as the sacrificial agent [29]. Brahimi R combined $CuCrO_2$ with TiO_2, produce hydrogen in acid solution [30].

However, to the best of our knowledge, it is hard to experimentally gain the delafossite ABO_2 materials with excellent photocatalysis because of the structural diversity. Therefore, it is essential to predict the structures and properties of delafossite ABO_2 materials by using first-principle calculations, which will greatly help the studies in this field. The goal of this work is to give a detail study of stabilities, electronic, bonding and optical properties of various delafossite ABO_2 materials and to obtain the potential candidates for photocatalytic applications. We will give the technical details of the computational methodology, as well as the geometry optimization, electronic properties, optical properties of the Ag and Cu based ABO_2 materials.

Theory

Computational methodology

We performed density-functional theory calculations with PAW potentials using the Perdew, Burke, Emzerhof (PBE) functional [31] (a common generalized gradient approximation functional) as implemented in the Vienna ab initio software package (VASP) [32–35]. The ionic cores are represented by PAW potentials, and calculations are non-spin-polarized. The VASP calculations used a 5×5×5 *k*-mesh by the Monkorst–Pack method with a 570 eV cutoff energy for plan-wave basis set. For delafossite structure optimization [36], the maximum force, the maximum stress and the maximum displacement are assured as 0.001 eV/Å, 0.001 Gpa, and 5.0×10^{-4} Å respectively.

Once optimized geometry structures were found, single point calculations were performed to obtain accurate electronic structures. Nb, Ta, V, Mg, Bi, Co, Zn, Ni, and Sb were used to construct initial delafossite ABO_2, some of which are transition metal having d states without being filled with electrons. Hence, in order to get more accurate electronic state, a *U* correction was used in this work [37,38]. We used a *U* value of 2.04 eV applied to Nb, 2.05 eV to Ta, 2.72 eV to V, 3.41 eV to Co, 6.50 eV to Zn, and 7.05 eV to Ni, which is similar to the values utilized in previous work [39–42].

The structural stability

Except for geometry optimization, the elastic properties of materials are important because they provide information on interatomic potentials and relate to various fundamental solid state phenomena such as mechanical stability and equations of state [43,44]. Elastic constants are defined by means of a Taylor expansion of the total energy, and it is obtained by calculating the total energy as a function of strain for hydrostatic and traceless hexagonal distortions. We used a combination of first-principle method and the tensor transformation method of Martin [45].

For delafossite structures (hexagonal structure), there are five dependent components of elastic constants C_{11}, C_{12}, C_{13}, C_{33}, and C_{44}. These elastic components can be calculated by means of volume conserving hexagonal distortions of the types for stiffness matrix [46].

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{(C_{11}-C_{12})}{2} \end{bmatrix} \quad (1)$$

The mechanically stable structures are dependent on the Born stability criteria [47,48], which are expressed as follows:

$$C_{44}>0,\ C_{44}>0,\ C_{11}-|C_{12}|>0,\ (C_{11}+2\times C_{12})\times C_{33}-2\times C_{33}^2>0 \quad (2)$$

It indicates that the ABO_2 structures are mechanically stable if it can be seen that these criteria of it are satisfied. Moreover, in order to determine the dynamical stability of the delafossite structure [49,50], we calculate the phonon spectrum of Brillouin zone center and all of the boundaries for the relaxed ABO_2 structures using the VASP code and Phonopy spectrum software [51].

In order to access the phonon information, we created a 2 × 2 × 1 supercell with 192 atoms by the different atomic displacement patterns along ten high-symmetry points (Γ-X-Y-Σ-Γ-Σ_1-N-P-Y_1-Z) in the whole Brillouin zone (BZ). We calculated the total energies with respect to displacements of atoms for the related structures along the line connecting high-symmetry points and obtained the phonon frequencies. The ABO_2 delafossite structures that have no imaginary frequency in the BZ are dynamically stable.

The electronic properties

To use solar irradiation efficiently, we sought ABO_2 delafossite structures with high reactivity under visible light (380 nm–760 nm). The semiconductors whose band gap is less

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