Applied Catalysis B: Environmental 225 (2018) 273–283

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Sulfide oxide XZnSO (X = Ca or Sr) as novel active photocatalytic water splitting solar-to-hydrogen energy conversion

A.H. Reshak

New Technologies – Research Centre, University of West Bohemia, Univerzitni 8, 306 14 Pilsen, Czech Republic

ARTICLE INFO

Keywords:
Photocatalytic
CaZnSO
SrZnSO
Transport properties
DFT
Non-centro-symmetric

ABSTRACT

The photocatalytic, structural and transport properties of the newly synthesized sulfide oxide CaZnSO and SrZnSO compounds are comprehensively investigated by means of first and second-principles calculation in order to explain the semiconductor's ‘photo-excitation' state mechanism in CaZnSO and SrZnSO. At the same time, the influence of the substitution of Ca^{2+} by Sr^{2+} on the structural properties and, hence, on the photocatalytic properties, are investigated. The optical conductivity and the absorption level exhibit an obvious enhancement from the ultraviolet to the visible light region when we move from Ca to Sr. This shows that the absorption edge moves from $\lambda = 387.4 \rightarrow \lambda = 442.7$ nm, which corresponds to the direct optical band gap of 3.2 eV → 2.8 eV, which is well matched with the solar spectrum and the sufficient negative conduction band potential for reduction of H^+/H_2. The calculated electronic band structure and the angular momentum character of various structures confirm that CaZnSO and SrZnSO possess a direct fundamental energy band gap of about 3.7 eV (CaZnSO) → 3.1 eV (SrZnSO), and the electronic charge distribution reveals a clear map of the electronic charge transfer and the chemical bonding. Furthermore, the carrier concentration (n) as a function of chemical potential at three constant temperatures (T) and n as a function of T at fixed chemical potential were calculated. It was found that n increases exponentially with increasing T and reveals that the CaZnSO and SrZnSO are p-type semiconductors. Based on these results, one can conclude that CaZnSO and SrZnSO satisfied all requirements to be an efficient photocatalyst. This will greatly improve the search efficiency and greatly help experiments to save resources in the exploration of new photocatalysts with good photocatalytic performance.

1. Introduction

Due to control of the electronic communication between the oxide and chalcogenide layers in a transition metal, the layered oxychalcogenides exhibit novel and unusual properties which is not possible to access in the oxides or chalcogenides [1]. The ordering of two anions in the crystal results in a layered crystal structure, which causes significant influence on the electronic properties [2,3]. It has been reported that the local electric polarity of CoS_3O, FeS_3O and ZnS_3O tetrahedra which was observed in transition metal oxychalcogenides CaCoSO, CaFeSO and CaZnSO, respectively, can influence the linear and nonlinear optical properties and the magnetic properties [3–6]. Recently, Sambrook et al. [3], have synthesized pure CaZnSO in a non-centrosymmetric hexagonal space group (P63mc) with two formula per unit cell. They reported that lattice constants are **a** = 3.75726(3) Å and **c** = 11.4013(1) Å, and that replacing Ca^{2+} with Sr^{2+} in CaZnSO causes the introduction of a different chemical pressure which in turn influences the polarity of the crystal structure, energy band gap and hence the optical properties. At the same time, they asserted that it is not possible to synthesize SrZnSO [3]. Very recently, Liu et al. [2] succeeded in synthesizing a novel polar SrZnSO in a non-centrosymmetric hexagonal space group (P63mc) with lattice constants a = 3.90442(6) Å and c = 11.6192(2) Å. They found that the SrZnSO is isostructural to CaZnSO, but is less polar than CaZnSO. They described the structural properties of SrZnSO. Therefore, as a natural extension to the work of Liu et al. and Sambrook et al., we have addressed ourselves to investigating the electronic band structure, density of states, electronic charge density distribution, photophysical and photocatalytic properties and thermoelectric properties of SrZnSO and CaZnSO using the first and second-principles methods. It has been reported that ZnS [7–11] and ZnO [12–17] are promising photocatalytic H_2 production materials under visible light irradiation. Therefore, we have addressed ourselves to investigating the photocatalytic performance of SrZnSO and CaZnSO as ZnS and ZnO-containing materials. It is well known that ZnS and ZnO generate electron-hole pairs by photoexcitation immediately and their extraordinary photostability is due to the highly negative reduction potentials of those excited electrons.

In recent years, due to the improvement of computational

E-mail address: maalidph@yahoo.co.uk.

https://doi.org/10.1016/j.apcatb.2017.12.006
Received 18 September 2017; Received in revised form 10 November 2017; Accepted 2 December 2017

technologies, it has been proven that the first-principles calculation is a strong and useful tool to predict the crystal structure and properties related to the electron configuration of a material before its synthesis [18–26]. It is well known that the DFT approaches have the ability to accurately predict the ground state properties of the materials, and the developed analysis tools are vital to investigating their intrinsic mechanism. It is anticipated that first-principle material approaches will greatly improve the search efficiency and greatly help experiments aimed at saving resources in the exploration of new materials with good performance [18–26]. For instance, several researchers have used the DFT calculation for exploration of new photocatalysts and found good agreement with experimental results [27–33]. We would like to mention that, in our previous work [34–37], we have calculated the photocatalytic properties and the energy band gaps using the full-potential method for several systems whose photocatalytic and energy band gaps are known experimentally, and a very good agreement with the experimental data was obtained. Thus, we believe that our calculations reported in this paper will produce very accurate and reliable results. The aim of this work is to focus on the photocatalytic activity of non-centro-symmetric CaZnSO and SrZnSO as new, green and efficient photocatalysts.

2. Structural aspects and methodology

The crystal structure of CaZnSO (SrZnSO) has polar layers in the *ab* plane of S atom-vertex-sharing ZnS_3O tetrahedral that are separated by Ca (Sr) ions of the (CaS_3O_3) (SrS_3O_3) octahedral [2], see Fig. 1. Sambrook et al. [3] reported that the substitution of Ca^{2+} (radii = 180 pm) by larger Sr^{2+} (radii = 200 pm) in CaZnSO introduces a different chemical pressure, which can change the structural polarity and reduce the fundamental energy band gap from 3.7 eV [3] to 3.1 eV [2], resulting in enhancing the optical activity. Therefore, to investigate the suitability of CaZnSO and SrZnSO for use as active photocatalysts, *ab initio* first-principle calculations are performed utilizing the full-potential method (wien2k code [38]) within the generalized gradient approximation (PBE-GGA) [39] to optimize the experimental lattice constant and the experimental atomic positions [2]. The lattice constants and the atomic positions obtained are listed in Table S1 and S2 (supplementary materials) in comparison with the available experimental data [2,3]. The recently modified Becke-Johnson potential (mBJ) [40] is used to calculate the ground state properties. The thermoelectric properties of CaZnSO and SrZnSO are obtained from the ground state within the limits of Boltzmann theory [41–43] and the constant relaxation time approximation as implemented in the BoltzTraP code [44].

In order to achieve energy eigenvalue convergence, the wave functions in the interstitial region are expanded using plane waves with a cutoff of $R_{MT} \times K_{max} = 7.0$, where K_{max} is the plane wave cut-off, and R_{MT} is the smallest of all atomic sphere radii. The charge density was Fourier expanded up to $G_{max} = 12(a.u.)^{-1}$. The maximum $\boldsymbol{l}$ value for

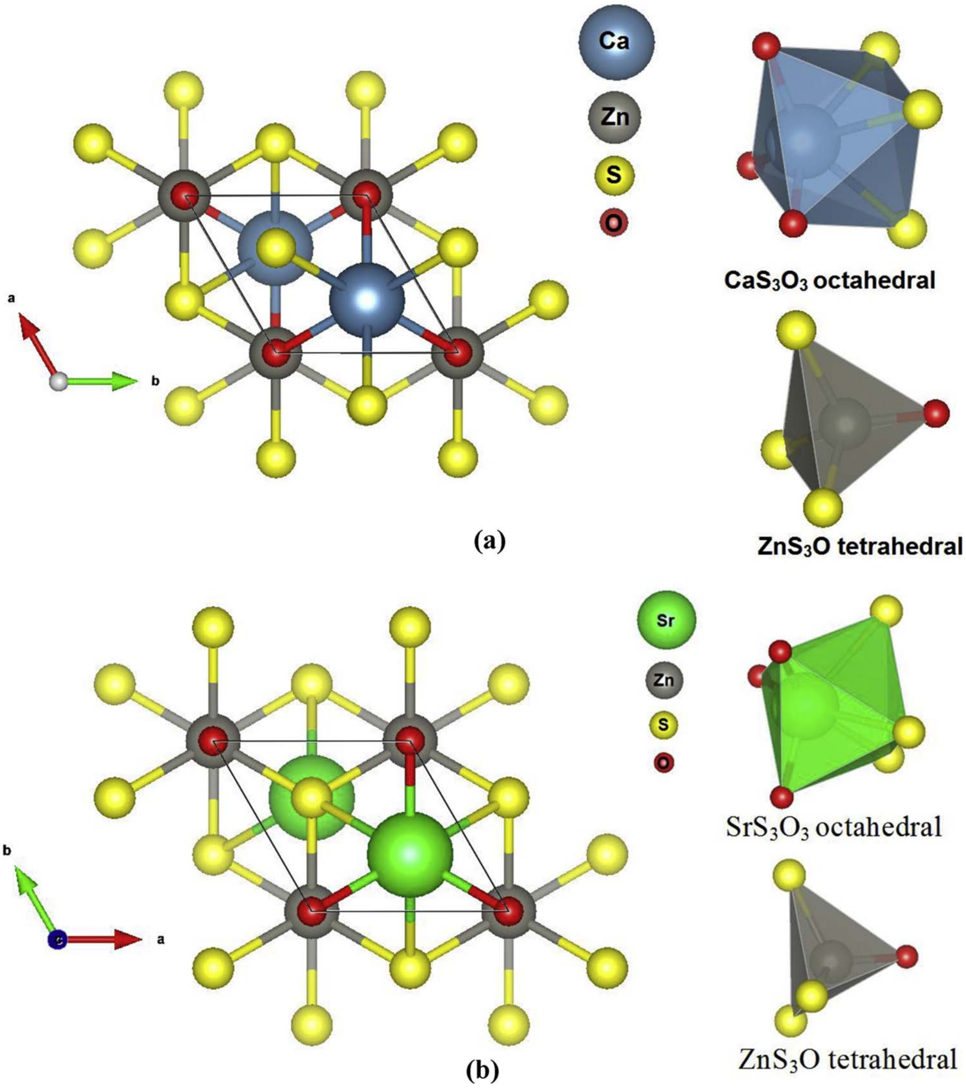

Fig 1. (a, b) Crystal structure of CaZnSO and SrZnSO; The crystal structure of CaZnSO (SrZnSO) has polar layers in the *ab* plane of S atom-vertex sharing ZnS_3O tetrahedral that are separated by Ca (Sr) ions of the (CaS_3O_3) (SrS_3O_3) octahedral.