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A comprehensive DFT study of physical and photocatalytic properties of $Sr_{1-x}Cd_xTiO_3$

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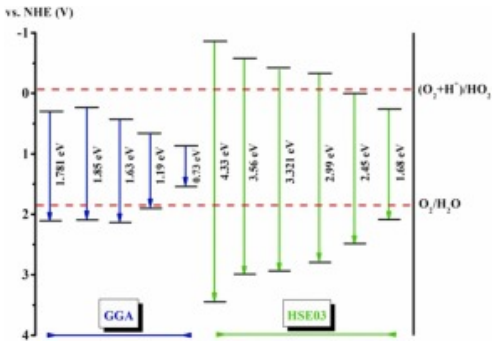
Abstract

Energy production from economic sources is a matter of concern for the last decade. Motivating from this, different properties of pristine and cadmium-induced $SrTiO_3$ are probed using first-principles calculations to predict a material for applications, including hydrogen production through water splitting and optoelectronic devices. Cd substituted at Sr site revealed to be more booming than Ti, as brand new gamma points emerged, impacting the electronic formation of pure $SrTiO_3$ by reducing band gap from 1.78 to 0 eV (GGA) and from 4.326 to 1.68 eV (HSE03). Fermi level shifted to near valence band in Cd substitution, revealing p-type property of semiconductor material. Subsequently, mechanical properties resulting from elastic constants were established, and these materials were finally established to justify the requirements for Born's stability. We evaluated and compared optical properties of pristine $SrTiO_3$ with Cd-loaded $SrTiO_3$, such as refractive index (3.62), dielectric function, and other optical properties. Pristine and Cd-$SrTiO_3$ play a vital role in hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and overall water splitting. The studied materials are claimed to be not only lead-free for green energy applications in photocatalytic activity, but also have a band gap range that is ideal for solar cell applications.

Graphical Abstract



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Introduction

The use of fossil fuel energy and industrial revolutions pose a major threat to the global ecosystem [1]. Photocatalytic water splitting utilizing sunlight with reusable photocatalyst material can limit reproduction of unnecessary by-products or toxic waste, in addition to reducing global warming [2], [3], [4]. Although photocatalysis materials have been widely explored (both experimentally and theoretically), effective photocatalysts remain a research priority. Although several methods based on electrolysis, thermochemical process, and bio-hydrogen production via bacteria/algae have been employed in the long-term production of hydrogen, such as Honda and Fujishima's TiO_2-based work in the 1970s [3]. Because optical band gaps of most metal-oxide photocatalysts, including perovskites, are too wide in the case of visible light regions, various efforts have been made to reduce them via chemical inclusion.

Cd is one of the most important II-VI semiconductors, being extensively explored for a variety of applications, including visible-light-driven photocatalysis [5], [6], [7], [8], [9], [10], [11], [12]. However, the photocatalytic effectiveness of Cd is substantially hampered by the quick recombination of the excited electron-hole pairs [6]. In addition, when photocatalytic processes are carried out in aqueous media, Cd is oxidized by the photogenerated holes, resulting in photo-corrosion [5], [7], [8], [9], [10]. Several ways have been devised to address these issues, including combining Cd with other semiconductors [7], [11], [13], conductive polymers [14] or carbon nanomaterials [15], [16], and these efforts have shown to be somewhat successful in terms of enhancing photoactivity and anti photo-corrosion.

Other researchers explored (La, Ag) inclusion of $CaTiO_3$, Sn, Ga) [17] codoping of $BiFeO_3$ [18], as well as (W, Fe/Mo) insertion of $BiVO_4$ [19], [20]. Researchers are still interested in water molecules splitting from a photocatalytic process in the visible solar spectrum, which is based on solar radiations. Overall, water splitting necessitates the use of a photocatalyst for redox processes involving hole reduction and water oxidation. As a result, materials such as phosphide, chalcogenide, nitride, many solid-state oxides, and carbide have been described in the literature [21], [22], [23], [24]. Researchers are now looking forward to the photocatalytic properties of Perovskite.

Photocatalysis produces hydrogen by converting photo-generated holes and electrons into a substance that undergoes a rapid oxidation and reduction process. As a result, photocatalyst efficiency is determined by the site of valence band (VB) and conduction band (CB) edges concerning redox potential of water. CB edge value must be lower than hole reduction potential, which is conduction band energy $H^+/H_2 \leq 0$ 0eV; similarly, the VB edge value must be higher than water oxidation potential, which is valance band energy

$H_2O/O_2 \geq 1.23$ eV. Any material with a band gap greater than 1.23 eV and a lower recombination rate for photogenerated electron-hole pairs can be a contender for executing the above-mentioned processes as well as splitting total water molecules [25]. A cost-effective and energy-efficient photocatalyst should have exceptional absorption capabilities in the visible to an ultraviolet range of electromagnetic spectra, allowing for practical use of solar radiation in large quantities.

The electronic band structure of cubic perovskite oxide ABO_3 may be adjusted, making it suitable for use in solar radiation electromagnetic spectra [26], [27]. This could be because the CB/VB of STO has St-4*d*, O-2*p* phases, which have a greater energy band gap. For photocatalytic applications, large band gap of $SrTiO_3$ (STO) is a drawback. To dynamically resize band gap and enhance absorption to visible spectra, cation insertion has been studied. Codoping techniques have been explored that ensure charge compensation and prevent formation of localised states. At ambient temperature, STO is a perovskite having a band gap of 3.2 eV that can split water into O_2 and H_2 without an exterior electric field [28], [29]. A wide band gap, on the other hand, necessitates ultraviolet energy, which accounts for only 3% of the solar spectrum. Anion concentration by adjusting the O-2*p* subjugated VB and cation insertion by manipulating the Ti-3*d* conquered CB are two strategies for overcoming this challenge. Because both of these techniques are hampered by development of localised donor or acceptor stages [30], [31], inclusion strategies have been studied. Because electronegativities of participating elements dictate band edge energy, we investigate a codoping method in this contribution in quest of an effective visible light active photocatalyst.

Because of its band gap engineering, Cd-STO is also suited for solar cells and other optoelectronic applications. This material is expected to shape the future of optoelectronic devices. Different concentrations of Cd-STO are provided in this paper. Trends in the band gap, optical, and elastic characteristics of all of these materials are also shown for pure and Cd-induced STO. The shifting of states towards lower energy is reflected in density of states (DOSs). Overall water-splitting efficiency of Cd-doped $SrTiO_3$ is eye-catching. The relevant sections include a full description of structural, electrical, elastic, mechanical, and optical responses.

Section snippets

Computational method

Heyd–Scuseria–Ernzerhof hybrid function (HSE03) and generalised gradient approximation using Perdew-Burke Erzenhoff (PBE) (GGA-PBE) implemented in Cambridge Serial Total Energy Package (CASTEP) using Ultra-soft pseudo-potential (USP) to consider electron exchange interaction were used to complete first-principles study [36]. Kohn-Sham equations were used to determine the effects of Cd-$SrTiO_3$ on material properties such as structural, optical, electrical, mechanical, elastic and photocatalytic…

Structural analysis

Geometry optimization is accomplished using a supercell to reduce outer effect before doing single-point computations for all studied properties. Lattice parameter is a key parameter that is also linked to band gap (E_g) since electronic band gap is linked to transitions between anions and cations and, as a result, to the inter-atomic distance between them. For pure $SrTiO_3$, lattice parameters equal to a=b=c= 3.95 Å are obtained through a correct modification of Birch-Murnaghan equation of state …

Conclusion

Structure, elastic, mechanical, electronic, optical characteristics and photocatalytic properties of pristine and Cd-$SrTiO_3$ have been studied using DFT. Both end materials were found to be cubic in nature and stable as well. E_g of pure STO is shown to be in good agreement along with theoretical and experimental value. Due to charge compensation, Cd inclusion avoids gap defect states. Cd inclusion leads to minimum E_g but energetical position of CB edge prevents photocatalytic water splitting…

CRediT authorship contribution statement

Muhammad Naeem: Conceptualization and Calculation. **M. Rizwan:** Study Design and Calculation. **Zahid Usman:** Data Analysis and Interpretation. **A. Imran:** Data Analysis and Interpretation. **Chuanbao Cao:** Data Analysis and Writing….

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.…

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