

Metal-ion dependent band energetics in $\text{SrM}_{0.5}\text{Ti}_{0.5}\text{O}_3$ (M = Ru, Rh, Ir, Pt, Pd) like structures for solar applications

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We present here a detailed comparative study of the theoretically-calculated electronic structures of the cubic $\text{SrM}_{0.5}\text{Ti}_{0.5}\text{O}_3$ (M: Ru, Rh, Ir, Pt, Pd) type and SrTiO_3 system. A their full potential linearized augmented plane wave (FP-LAPW) method was used to obtain its band structure within the framework of a density functional theory by using Wien97 code. The 4d orbitals of Ru, Rh and 5d orbitals of Ir, Pt respectively, contribute to the top of the valence band yielding a band gap narrowing of cubic SrTiO_3 . The computed tolerance factor for the $\text{SrTi}_{0.5}\text{Pd}_{0.5}\text{O}_3$ perovskite structure indicates an unstable structural formation with Pd metal ion. The computation of the frequency-dependent absorption coefficient $I(\omega)$ of $\text{SrTi}_{0.5}\text{M}_{0.5}\text{O}_3$ indicates that Rh has a significant absorption efficiency for low energy ($E \leq 2\text{eV}$) photons, whereas Ru and Ir display a very high absorption efficiency for photons with $E > 2\text{eV}$. Theoretical prediction validates that Rh can yield a better solar photoactive material than Ru and Ir in the $\text{SrTi}_{0.5}\text{M}_{0.5}\text{O}_3$ (M:Ru, Rh, Ir) type system for low energy photon applications.

Key words: $\text{SrM}_{0.5}\text{Ti}_{0.5}\text{O}_3$, FP-LAPW Method, SrTiO_3 , Solar Photoactive Material, Partial Density of States.

Introduction

Recently we reported hydrothermal synthesis of doped perovskite nanoparticles viz. $\text{SrTi}_x\text{M}_{1-x}\text{O}_3$ (M : Ru, Rh, Ir, Pt, Pd) and demonstrated that noble metal doping renders visible light photocatalytic activity in SrTiO_3 [1]. The titanate of strontium is one of the potent photocatalysts that exhibits photocatalytic properties very similar to titanium dioxide [1, 2, 3]. Although like TiO_2 , SrTiO_3 offers the advantages of significantly good photocatalytic efficiency and stability under UV light radiation, however its large bandgap ($\sim 3.2\text{ eV}$) is a limitation for its visible light photo-catalysis applications. The possibility to modify a wide band gap material to one that absorbs low energy photons [3, 4] is thus an important issue and needs special attention. This becomes more important and critical in the case of doped metal oxides where a very low noble metal concentration can induce such desirable optical properties. Thus, in order to improve the understanding of noble metal ion doped SrTiO_3 (STO) we attempt the present study.

The knowledge of the electronic and optical structure enables one to judge the potential of a material for opto-electronic applications [5]. Strontium titanate exhibits a

cubic perovskite structure with $Pm3m$ space group at room temperature. It consists of a central Ti^{4+} -ion, which is octahedrally coordinated by 6 O^{2-} , and 8 Sr^{2+} ions situated at the corner of the cube. The large band gap of this efficient and stable photocatalyst needs modification of the optical properties for its utilization in visible light photocatalysis. Doped perovskite offer such an advantage by virtue of band gap tuning, thereby showing a red shift in the optical absorption of the UV-active original host lattice [4]. The present study is one of the few attempts where the noble metal doped STO system has been explored for a deeper understanding of the physico-chemical properties. Here we calculated the electronic structure for the cubic perovskite structure of SrTiO_3 , $\text{SrTi}_{0.5}\text{M}_{0.5}\text{O}_3$ (M : Ru, Rh, Ir, Pt) like structure, and further we have also calculated their respective optical properties to qualitatively understand the possible role of the material for solar energy application. In addition, the report correlates the experimental observations to narrate the candidacy of the system for visible light photocatalysis.

This paper is described in three sections (i) calculation of electronic band structures of SrTiO_3 , $\text{SrTi}_{0.5}\text{M}_{0.5}\text{O}_3$ (M:Ru, Rh, Ir, Pt)-type cubic perovskite lattice, (ii) calculation of respective optical property, and (iii) qualitative evaluation of computed properties of SrTiO_3 , $\text{SrTi}_{0.5}\text{M}_{0.5}\text{O}_3$ (M : Ru, Rh, Ir, Pt) like structure as a solar energy material.

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Experimental

Theoretical calculations were performed with the full potential linearized augmented plane-wave (FP-LAPW) method as implemented in the Wien97 code within a density functional theory (DFT) in a generalized gradient approximation (GGA) [6]. In the FP-LAPW method the unit cell is divided in two types of regions, the atomic spheres centred upon nuclear sites and the interstitial region between non-overlapping spheres. The potential and charge density are expanded into lattice harmonics and as a Fourier series. Thus it is completely general, with no shape approximation for the potential. The muffin-tin radii for Sr, Ti (M) and O were chosen to be 2.0, 1.8 (1.6) and 1.6 a.u. respectively in these calculations. The convergence parameter RK_{max} was set to 6.0. Calculations were carried out with the experimental lattice constant. The atomic coordinates were adopted from literature [1]. For self-consistency, the charge convergence criteria of 0.0001 a.u. was used. The integrations were carried out on a 18 k -point mesh in the irreducible Brillouin zone (BZ) for the STO. Further a fine mesh of 102 k -points in the irreducible BZ of the cubic unit cell was used to calculate the frequency-dependent absorption coefficient $I(\omega)$ from real and imaginary parts of the dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$. A procedure similar to Gupta *et al.* [7], and Borse *et al.* [8,9] was followed for the calculation of $I(\omega)$ which is given as $I(\omega) = \sqrt{2}(\omega)(\sqrt{\epsilon_1(\omega)^2 + \epsilon_2(\omega)^2} - \epsilon_1(\omega))^{1/2}$.

Results and Discussions

The input crystallographic data of STO was adopted from the literature [10]. A fictitious cell with two STO units was constructed for the band structure calculations of the cubic $\text{SrM}_{0.5}\text{Ti}_{0.5}\text{O}_3$ ($M : \text{Ru}, \text{Rh}, \text{Ir}, \text{Pt}, \text{Pd}$) type system. Fig. 1 shows a schematic of such a fictitious cell ($\text{SrTi}_{0.5}\text{M}_{0.5}\text{O}_3$ ($M : \text{Ru}, \text{Rh}, \text{Ir}, \text{Pt}$)) in the form of cubic double unit cell along with the crystal structure of cubic SrTiO_3 . In the case of each system, an M-ion was substituted for the titanium ion and further used for the computation of the respective electronic structure and optical property. The cubic STO structure belongs to the $Pm\bar{3}m$ space group (space group no. 221) and has a lattice constant of $a = 3.905\text{\AA}$. We find in the present study that the electronic structure of the $\text{SrM}_{0.5}\text{Ti}_{0.5}\text{O}_3$ (*i.e.* $x = 0.5$) type system serves as a qualitative guide for the electronic structure for other member candidates of $\text{SrM}_x\text{Ti}_{1-x}\text{O}_3$ for $x < 0.5$ as well as $x < 1$, the calculation of which otherwise will require a large supercell and advanced hardware to handle such a computation. The theoretical feasibility of the $\text{SrM}_{0.5}\text{Ti}_{0.5}\text{O}_3$ perovskite structure formation was confirmed for the metal ions of $M : \text{Ru}, \text{Rh}, \text{Ir}, \text{Pt}, \text{Pd}$ [11]. The tolerance factor indicated theoretically, the formation of a stable structure except in the case of palladium. This was also observed in the

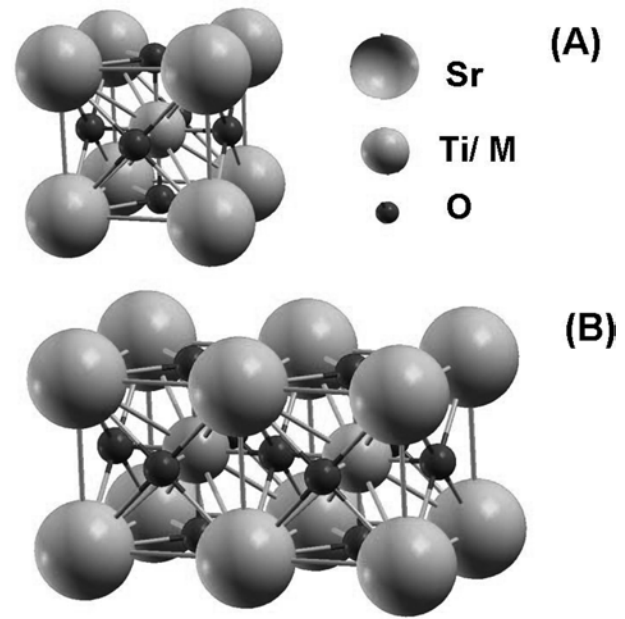


Fig. 1. Schematic showing the crystal structure of (a) Cubic SrTiO_3 and (b) cubic, double unit cell of $\text{SrTi}_{0.5}\text{M}_{0.5}\text{O}_3$ ($M : \text{Ru}, \text{Rh}, \text{Ir}, \text{Pt}$) type system that was used for the computational work.

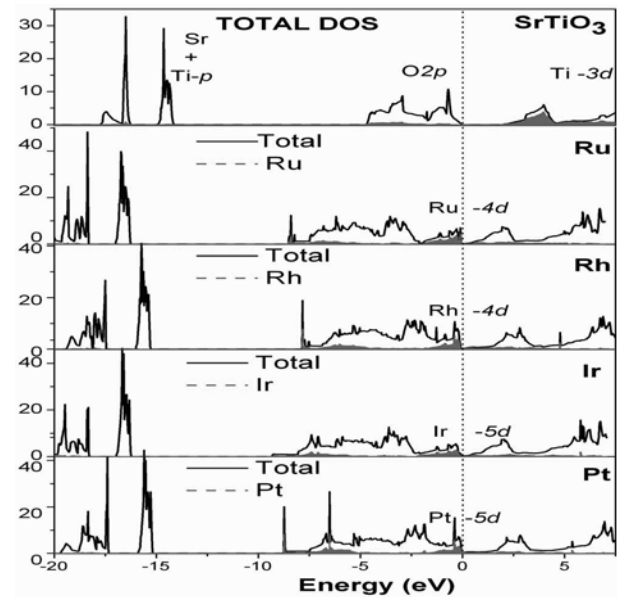


Fig. 2. Total and partial DOSs of SrTiO_3 and $\text{Sr}(\text{M}_{0.5}\text{Ti}_{0.5})\text{O}_3$ illustrating the effect of the metal ion (M) on the DOS of STO. The unit of each vertical axis is states/(eV/unit cell). The Fermi level is set at 0 eV in each case.

experimental studies thus supporting the theoretical hypothesis of the present studies.

Fig. 2 shows the computed total and partial density of states (DOSs) for cubic STO and $\text{Sr}(\text{M}_{0.5}\text{Ti}_{0.5})\text{O}_3$ type systems. It demonstrates that there is a subsequent effect on the total DOS due to the substitution of a metal ion in the $\text{Sr}(\text{M}_{0.5}\text{Ti}_{0.5})\text{O}_3$ lattice. The main observation is that in all cases the M states, viz., 4d (for Ru and Rh)

and 5d (for Ir and Pt), mainly contribute to the top of the valence band in $\text{Sr}(\text{M}_{0.5}\text{Ti}_{0.5})\text{O}_3$, thereby narrowing the band gap as compared to the experimental band gap of STO (eV). Further there is an increase in the Fermi energy and widening of the valence band width (the calculated value) for the M ions with reference to the STO. Further analysis reveal that in all cases of $\text{Sr}(\text{M}_{0.5}\text{Ti}_{0.5})\text{O}_3$ the low energy DOS in the range of -20 to ~ -12 eV has the main contribution of Sr-d and Ti-p states. The high energy DOS near the valence bands are dominantly constituted of O2p. The high energy DOS above the Fermi energy (E_F) mainly Ti 3d orbitals contribute to the conduction band of STO. Likewise, for $\text{Sr}\text{M}_{0.5}\text{Ti}_{0.5}\text{O}_3$, (i) respective 4d states for $M = \text{Ru}$ and Rh and (ii) 5d states of Ir and Pt additionally contribute to the top of the valence band thereby increasing the valence band width and effectively reducing the band gap of the M systems. Consequently, M is substituted at the B-site of ABO_3 system; there is a dramatic band gap alteration in the $\text{Sr}(\text{M}_{0.5}\text{Ti}_{0.5})\text{O}_3$. Such a kind of doping is known to narrow the band gap of the host lattice. Thus such a band gap tuning can be effectively useful in solar light absorption.

Fig. 3 displays the results of the comparison of the computed energy-dependent absorption coefficient $I(\omega)$ for STO and the doped STO systems in the range of energy from 0-10 eV that includes the low energy visible rays as well as high energy UV rays. The trend in the variation shows that Rh has the largest $I(\omega)$ at lower energies than all the others, thus indicating ability to respond to low energy ($E < 2.0$ eV) photons. The $I(\omega)$ curves for $\text{Sr}(\text{M}_{0.5}\text{Ti}_{0.5})\text{O}_3$ doped type systems are significantly different from that of STO, with the main difference that the optical response of the doped system is either enhanced and/or red shifted with reference to

the optical response of STO. Specifically, $\text{Sr}(\text{M}_{0.5}\text{Ti}_{0.5})\text{O}_3$ systems with M as Rh and Pt display significant absorption coefficients than STO in the low energy range of 0-2 eV. These results of optical property calculation clearly reveal that $\text{Sr}(\text{M}_{0.5}\text{Ti}_{0.5})\text{O}_3$ systems with M as $\text{Rh} > \text{Pt} > \text{Ru} > \text{Ir}$ in decreasing order of response depending on the $I(\omega)$ response to visible or near UV electromagnetic radiation in a rather more efficient manner than cubic undoped STO.

The physical significance of this work can be understood by detailed analysis of the above results. Accordingly, the results are discussed in this section to explain the application of the doped system in solar energy conversion applications. Table 1 shows the computed band gap as well as flat band potential values for $\text{Sr}(\text{M}_{0.5}\text{Ti}_{0.5})\text{O}_3$ systems [5]. Firstly, the band gap value of each respective system reveals that the theoretical band gap is narrowed as compared to the observed band gap of undoped STO. Secondly, the closeness of the flat band potential values to that of STO makes it a more suitable candidate for hydrogen production. The band gap narrowing in the doped STO system indicates that the M-system can absorb the visible radiation of the electromagnetic spectrum. The computed theoretical band gap value of $\text{Sr}(\text{M}_{0.5}\text{Ti}_{0.5})\text{O}_3$ can be treated as a validate indicator to conclude that there is a band gap alteration on the doping with M-ion. Nonetheless, if one can vary the value of $0 < x < 1$ in the $\text{Sr}(\text{M}_x\text{Ti}_{1-x})\text{O}_3$ system, one can easily tune the band gap to a desirable value. Thus the work gives a necessary qualitative picture of the possible effects of a dopant on the DOS with respect to the undoped counterpart system viz. STO. Next, the theoretical flat band potential values for all M's (except for $M = \text{Pd}$) shown in the Table I are very close to that of STO, that possesses a best suited reduction potential (i.e. suitable flat band potential) for photocatalytic reduction of water. Thus all the M-system in $\text{Sr}(\text{M}_{0.5}\text{Ti}_{0.5})\text{O}_3$ are predicted to be suitable for photocatalytic reduction of water. This is in agreement with the experimentally reported observations [1].

Our recent experimental observations do ensure that the doped M-system for $\text{Sr}(\text{M}_{0.5}\text{Ti}_{0.5})\text{O}_3$ systems showed altered band gaps for M as Rh (2.5 eV), Ru (2.0 eV), Ir (2.2 eV) and Pt (3.0 eV) with respect to the STO [1]. The present theoretical study validates that doping is a smart guideline to an experimentalist to achieve an

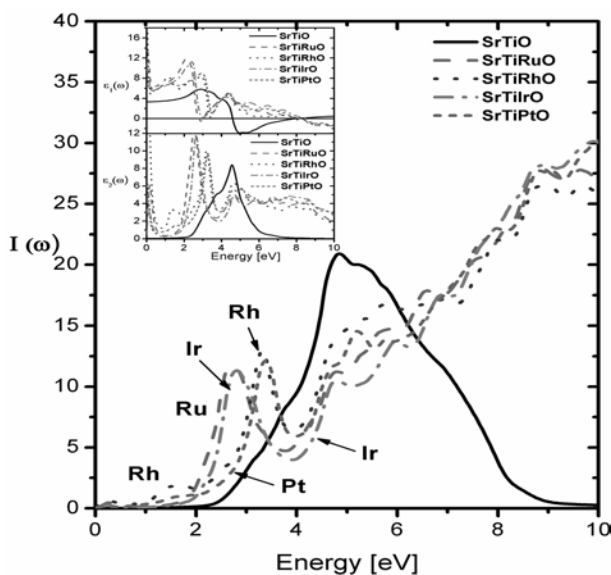


Fig. 3. Calculated absorption coefficient $I(\omega)$ of cubic SrTiO_3 and doped $\text{Sr}(\text{M}_{0.5}\text{Ti}_{0.5})\text{O}_3$ type structures, as a function of photon energy. Inset shows calculated the real and imaginary part of the dielectric function used for the calculation of $I(\omega)$.

Table 1. The computed band gap and flat band potential values for each $\text{Sr}(\text{M}_{0.5}\text{Ti}_{0.5})\text{O}_3$ system

$\text{Sr}(\text{M}_{0.5}\text{Ti}_{0.5})\text{O}_3$ for M	Theoretical band gap, E_g (eV)	Theoretical flat band potential E_{FB} (eV)
Rh	0.33	-5.04
Ru	0.49	-5.10
Ir	0.41	-5.13
Pt	0.19	-5.08
Pd	NA	NA
SrTiO_3	2.34	-4.97

optically-active material for solar applications.

The computed band gap of STO is found to be under estimated [12] to that of the experimentally reported band gap. In spite of such an underestimation of the computed band gap value, we believe that the present type of qualitative study is important on a relative scale especially for photocatalysis application. The correctness of the present computational and empirical approach is validated by the case study of TiO_2 a well known photocatalyst and our earlier reports. In addition we can easily observe that the doping has shown the expected effect on the important parameter of the flat band potential. As shown in the Table I, the M-ion doping in $\text{Sr}(\text{M}_{0.5}\text{Ti}_{0.5})\text{O}_3$ significantly controls the redox potential of the doped system along with the band gap, thereby giving an access to tailor the dopant-concentration dependent parameters. This enables one to fabricate a desirable photocatalysis for solar applications.

Although STO is a well known photocatalyst working at the photon energy > 3 eV, the computed optical absorption coefficient of $\text{Sr}(\text{M}_{0.5}\text{Ti}_{0.5})\text{O}_3$ clearly show that $M = \text{Rh}$ can be easily used under visible light photons, but not STO. Accordingly, Bae *et al.* have observed a significant activity for visible light photocatalysis [1] thus validating the expected fact of turning a UV-active photocatalyst (STO) to a visible active photocatalyst for $\text{Sr}(\text{M}_{0.5}\text{Ti}_{0.5})\text{O}_3$ with $M = \text{Rh, Ru}$ and Ir . It goes without saying that apart from suitable redox potential values, the optical response of these systems plays a major role in rendering a photocatalytic activity under photons with energy $E < 2.5$ eV. Furthermore, apart from the photochemical application Fig. 3, indicates that the optical response of $\text{Sr}(\text{M}_{0.5}\text{Ti}_{0.5})\text{O}_3$ for M can be arranged as $\text{Rh} > \text{Pt} > \text{Ru} > \text{Ir}$ order in decreasing order of optical response. Such optical behavior makes these materials possible candidates for solar applications.

Conclusions

The work describes the computational study of electronic

and optical properties of cubic SrTiO_3 and cubic $\text{Sr}(\text{M}_{0.5}\text{Ti}_{0.5})\text{O}_3$ for $M = \text{Rh, Ru, Ir, Pt}$ and Pd metal ions. The 4d (Rh and Ru) and 5d (Ir and Pt) orbitals contributed to the top of the valence band resulting in a band gap reduction of cubic SrTiO_3 . For these cubic $\text{Sr}(\text{M}_{0.5}\text{Ti}_{0.5})\text{O}_3$ type systems, the computed optical absorption coefficients indicate that $\text{Rh} > \text{Ru} > \text{Ir}$ can be arranged in decreasing order of photoresponse towards low energy photons of energy $E < 2.5$ eV.

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