



Final Report

Project title: Energy band gap engineering of perovskite oxides for photocatalytic hydrogen production from visible light: Theory and computations

By Asst. Prof. Pakpoom Reunchan

08 / 2017

Contract No. TRG5780260

Final Report

Project title: Energy band gap engineering of perovskite oxides for photocatalytic hydrogen production from visible light: Theory and computations

Researcher

1. Asst. Prof. Pakpoom Reunchan
2. Prof. Sukit Limpijumnong

Institute

Kasetsart University
Suranaree University of Technology

This project granted by the Thailand Research Fund

Abstract

Project Code : TRG5780260

Project Title : Energy band gap engineering of perovskite oxides for photocatalytic hydrogen production from visible light: Theory and computations

Investigator : Pakpoom Reunchan

E-mail Address : pakpoom.r@ku.ac.th

Project Period : 15 July 2014 to 14 July 2016

Abstract:

Density functional calculations are performed to investigate the effect of nitrogen (N) impurities on the optical properties of N-doped CaTiO_3 , SrTiO_3 and BaTiO_3 . The screened hybrid-functional proposed by Heyd, Scuseria, and Ernzerhof (HSE) is used to obtain the accurate band gaps, electronic structure and formation energies of the N impurities. In this project, we pay special attention to the energetics and optical properties of N impurities in SrTiO_3 , which is a promising candidate for hydrogen evolution under visible-light irradiation. Here, hybrid density-functional calculations are employed to investigate the stability and impact of nitrogen impurities on the electronic and optical properties in SrTiO_3 . We find that the substitutional N on O site (N_O) is a deep acceptor in SrTiO_3 . N_O predominates over other N-related defects under any equilibrium growth conditions in *n*-type SrTiO_3 . Our results reveal that N_O gives rise to visible-light absorption, in agreement with experimental observations. In addition, we find that hydrogen can bind to N_O , and that $\text{N}_\text{O}\text{-H}_i$ leads to a blueshift in the optical absorption. Other N configurations can also contribute to optical absorption in the visible range. The vibration frequencies of the different N configurations are provided to support identification by vibrational spectroscopy techniques.

Keywords : density-functional calculations, strontium titanate, doping, nitrogen

รหัสโครงการ : TRG5780260

ชื่อโครงการ: การออกแบบและปรับปรุงแถบช่องว่างพลังงานของเพอร์อฟสไกต์ออกไซด์เพื่อการผลิตไฮโดรเจนจากกระบวนการเร่งปฏิกิริยาดำเนินการในย่านที่ตามองเห็น: ทฤษฎีและการคำนวณ

ผู้วิจัยหลัก: ผศ.ดร. ภาคภูมิ เรือนจันทร์

อีเมล : pakpoom.r@ku.ac.th

ระยะเวลาโครงการ : เริ่มตั้งแต่ 15 กรกฎาคม 2014 ถึง 14 กรกฎาคม 2016

บทคัดย่อ:

ในโครงการวิจัยนี้การคำนวณโดยใช้ฟังก์ชันของความหนาแน่นถูกนำมาใช้ในการตรวจสอบคุณสมบัติเชิงแสงของรูปแบบของสิ่งเจือปนในโครงสร้างในแคลเซียมไททาเนต (CaTiO_3) สตรอนเทียมไททาเนต (SrTiO_3) และ แบเรียมไททาเนต (BaTiO_3) ฟังก์ชันแบบผสมที่ถูกกำหนดโดย Heyd, Scuseria และ Ernzerhof (HSE)

ถูกนำมาใช้ในการคำนวณเพื่อให้ได้มาซึ่งแถบช่องว่างพลังงานของสารประกอบเพอร์อฟสไกต์ที่แม่นยำขึ้น รวมถึงโครงสร้างทางอิเล็กทรอนิกส์ และพลังงานการก่อตัวของความบกพร่องที่เกี่ยวข้องกับไนโตรเจน ในโครงการวิจัยนี้ผู้วิจัยมุ่งเน้นไปที่การพลังงานของการก่อตัวและคุณสมบัติเชิงแสงของความบกพร่องและไนโตรเจนที่เจือปนเข้าไปในผลึก SrTiO_3

ซึ่งเป็นวัสดุที่มีศักยภาพสำหรับการผลิตไฮโดรเจนภายใต้การแผ่ของแสงในย่านที่ตามองเห็น

ในงานวิจัยนี้การคำนวณโดยใช้ฟังก์ชันแบบผสมถูกใช้ในการตรวจสอบเสถียรภาพและผลกระทบของไนโตรเจนที่เจือปนในผลึก SrTiO_3 ที่มีต่อคุณสมบัติเชิงอิเล็กทรอนิกส์และเชิงแสง

ผู้วิจัยพบว่าไนโตรเจนที่ไปแทนที่ออกซิเจน (N_O) เป็นตัวรับอิเล็กตรอนแบบลึก โดยที่ N_O

มีความเข้มข้นสูงกว่าความบกพร่องไนโตรเจนในรูปแบบอื่นๆในเงื่อนไขการปลูกผลึกภายใต้สมดุลเชิงความร้อนใน SrTiO_3 ที่เป็นชนิดเอ็น ผลการวิจัยแสดงว่า N_O

ทำให้เกิดการดูดกลืนแสงในย่านที่ตามองเห็นซึ่งสอดคล้องกับผลการทดลองที่รายงานออกมา

นอกจากนี้ยังพบว่าไฮโดรเจนอะตอมสามารถยึดเกาะกับ N_O กลายเป็นความบกพร่องแบบซับซ้อน $\text{N}_\text{O}-\text{H}$ และทำให้เกิดการเลื่อนไปทางสีน้ำเงินของการดูดกลืนแสง

รูปแบบของไนโตรเจนอะตอมที่เจือปนอื่นๆก็มีส่วนในการทำให้เกิดการดูดกลืนแสงในย่านที่ตามองเห็นได้เช่นกัน

ผู้วิจัยได้คำนวณความถี่การสั่นของไนโตรเจนในรูปแบบต่างๆเพื่อช่วยสนับสนุนการทดลองที่เกี่ยวข้องกับการวัดความถี่การสั่นอีกด้วย

2. Executive summary

We employed density-functional calculations to investigate the effect of nitrogen (N) impurities on the optical properties of N-doped CaTiO_3 , SrTiO_3 and BaTiO_3 . The screened hybrid-functional proposed by Heyd, Scuseria, and Ernzerhof (HSE) is used to obtain the accurate band gaps, electronic structure and formation energies of the N impurities. The Hatree-Fock exchange mixing parameters were adjusted to yield the experimental band gaps for each material. The lattice constants and heat of formations are in good agreement with the experimental values. The band alignments of the three perovskites are also provided. In this project, we pay special attention to the energetics and optical properties of N impurities in SrTiO_3 , which is a promising candidate for hydrogen evolution under visible-light irradiation. Here, hybrid density-functional calculations are employed to investigate the stability and impact of nitrogen impurities on the electronic and optical properties in SrTiO_3 . We find that the substitutional N on O site (N_O) is a deep acceptor in SrTiO_3 . N_O predominates over other N-related defects under any equilibrium growth conditions in *n*-type SrTiO_3 . Our results reveal that N_O gives rise to visible-light absorption, in agreement with experimental observations. In addition, we find that hydrogen can bind to N_O , and that $\text{N}_\text{O}\text{-H}_\text{i}$ leads to a blueshift in the optical absorption. Other N configurations can also contribute to optical absorption in the visible range. The vibration frequencies of the different N configurations are provided to support identification by vibrational spectroscopy techniques. The optical absorption associated with N_O in BaTiO_3 and CaTiO_3 were also calculated. We find that N_O in BaTiO_3 gives rise to visible-light absorption while that in CaTiO_3 leads to absorption near ultraviolet region.

3. Objective

(1) To systematically investigate the effects of N doping in SrTiO_3 , BaTiO_3 , and CaTiO_3 on the visible-light absorption through hybrid-density functional calculations. The special attention is paid on N impurities in SrTiO_3 .

(2) To develop the effective strategies for energy band gap engineering of SrTiO_3 , BaTiO_3 , and CaTiO_3 for enhancing the photocatalytic H_2 production from water splitting under visible-light irradiation.

4. Research methodology

Our density-functional calculations were employed using Vienna abinitio simulation package (VASP). To calculate the fundamental physical properties, we adopt the primitive cell containing 5 atoms of SrTiO_3 , BaTiO_3 or CaTiO_3 . For the Brillouin zone integrations, a set of $7\times 7\times 7$ *k*-point grid is used for SrTiO_3 , BaTiO_3 and $8\times 8\times 8$ *k*-point grid is used for CaTiO_3 . The energy cutoff of 400 eV is used for the plane-wave expansion for SrTiO_3 , BaTiO_3 and 500 eV for CaTiO_3 . The Heyd-Scuseria-Ernzerhof (HSE) hybrid functional was adopted in all calculations in which the the Hatree-Fock (HF) mixing parameters were determined to reproduce the experimental values. For SrTiO_3 , Sr $4s^2 4p^6 5s^2$, Ti $3d^3 4s^1$, O $2s^2 2p^4$ and the N $2s^2 2p^3$ were treated as valence electrons within the projector-

augmented wave (PAW) method. The use of the Hatree-Fock mixing parameter of 28% in the HSE approach yield an indirect band gap (R-) of 3.27 eV, in good agreement with the experimental value of 3.25 eV. The calculated lattice parameter of 3.913 Å, is very close to the experimental value of 3.905 Å for cubic SrTiO₃. The HSE functional has been widely adopted in studies of defects and impurities in wide-band-gap semiconductors, with overall excellent agreement between theory and experiment. The simulations of the N impurity employed a 90-atom supercell, which is a 3×3×2 repetition of the five-atom primitive cell of cubic SrTiO₃, and 2×2×2 mesh of special *k*-point. The energy cutoff for the planewave basis set expansion was set to 400 eV.

The likelihood of forming substitutional, interstitial or other configurations of the N impurity is determined by the formation energy as a function of oxygen (μ_{O}) and nitrogen (μ_{N}) chemical potentials, for all possible charge states. We calculated the thermodynamic transition level and optical transitions following the standard procedure described in Ref. For example, the formation energy of N_O in charge state q is given by:

$$E^f(\text{N}_\text{O}^q) = E_\text{tot}(\text{N}_\text{O}^q) - E_\text{tot}(\text{SrTiO}_3) - \mu_{\text{N}} + \mu_{\text{O}} + qE_F + \Delta^q \quad (1.1)$$

where $E_\text{tot}(\text{N}_\text{O}^q)$ is the total energy of the supercell containing one N substituted for an O site (N_O). $E_\text{tot}(\text{SrTiO}_3)$ is the total energy of the perfect crystal using the same supercell. The O atom that is removed from the supercell is placed in a reservoir with energy μ_{O} , referenced to the total energy per atom of an isolated O₂ molecule ($\mu_{\text{O}} = \tilde{\mu}_{\text{O}} + \frac{1}{2}E_\text{tot}[\text{O}_2]$), and the N atom is taken from a reservoir with energy μ_{N} , referenced to the total energy per atom of an isolated N₂ molecule ($\mu_{\text{N}} = \tilde{\mu}_{\text{N}} + \frac{1}{2}E_\text{tot}[\text{N}_2]$). The chemical potentials $\tilde{\mu}_X$ ($X = \text{Sr}, \text{Ti}, \text{O}, \text{N}, \text{H}$) are treated as variables and can be appropriately chosen to represent experimental conditions during growth or annealing. The Fermi level E_F is the electron chemical potential, referenced to the valence band maximum (VBM). We applied the charge-state dependent correction (Δ^q) due to the finite size of the supercell following the approach in Ref. [37]. Notably, however, Δ^q is very small, due to the large static dielectric constant of SrTiO₃. The formation energy of the other N configurations and N-H complexes in various charge states are obtained using similar procedure. The chemical potentials $\tilde{\mu}_{\text{Sr}}$, $\tilde{\mu}_{\text{Ti}}$ and $\tilde{\mu}_{\text{O}}$ must satisfy the stability condition of $\tilde{\mu}_{\text{Sr}} + \tilde{\mu}_{\text{Ti}} + 3\tilde{\mu}_{\text{O}} = \Delta H_f(\text{SrTiO}_3)$, where $\Delta H_f(\text{SrTiO}_3)$ is the enthalpy of formation of SrTiO₃; the calculated value is −16.2 eV. Their values are taken with respect to the total energy per atom of metallic Sr (fcc), metallic Ti (hcp) and O₂ molecule. Bounds are imposed to $\tilde{\mu}_{\text{Sr}}$, $\tilde{\mu}_{\text{Ti}}$ and $\tilde{\mu}_{\text{O}}$ in order to avoid formation of secondary phases. For example, the formation of SrO is prevented by taking into account the constraint: $\tilde{\mu}_{\text{Sr}} + \tilde{\mu}_{\text{O}} < \Delta H_f(\text{SrO})$. Similar constraints are applied to the formation of other relevant limiting phases: SrO₂, TiO₂, TiO and Ti₂O₃.²⁹ We present results of formation energies for O-rich, the intermediate, and O-poor conditions. The O-rich and O-poor conditions correspond to the oxygen chemical potential $\tilde{\mu}_{\text{O}} = 0$ and $\tilde{\mu}_{\text{O}} = (\Delta H_f(\text{SrTiO}_3) - \tilde{\mu}_{\text{Ti}} - \tilde{\mu}_{\text{Sr}}) / 3 = -5.27$ eV, respectively. For the intermediate condition, the O chemical potential was chosen to reflect the growth conditions in Ref. [16]. Based on a growth

temperature of 1100 °C and a pressure of 1 atm, we get $\tilde{\mu}_O = -1.57$ eV.⁸ Under O-rich and the intermediate (experimental) growth conditions, $\tilde{\mu}_N$ is limited by the formation of N_2 molecule, i.e., $\tilde{\mu}_N = 0$ while under O-poor (Ti-rich) growth condition, $\tilde{\mu}_N$ is limited by the formation of solid TiN, i.e., $\tilde{\mu}_N = \Delta H_f(\text{TiN}) - \tilde{\mu}_{\text{Ti}}$. Note that the formation of NO, N_2O , NO_2 molecules are not relevant in determining $\tilde{\mu}_N$ under any growth condition considered. Under O-rich and the experimental conditions, the solubility of H-related defects are limited by the formation of H_2O , i.e., $\tilde{\mu}_H = (\Delta H_f(H_2O) - \tilde{\mu}_O)/2$, while under O-poor conditions (metal-rich) the solubility is limited by the formation of solid SrH_2 , i.e., $\tilde{\mu}_H = (\Delta H_f(SrH_2) - \tilde{\mu}_{\text{Sr}})/2$. The allowed chemical potential values for $BaTiO_3$ and $CaTiO_3$ were obtained following the similar procedure. The chemical potential diagram for the stable growth of $SrTiO_3$ is shown in Fig. 1.

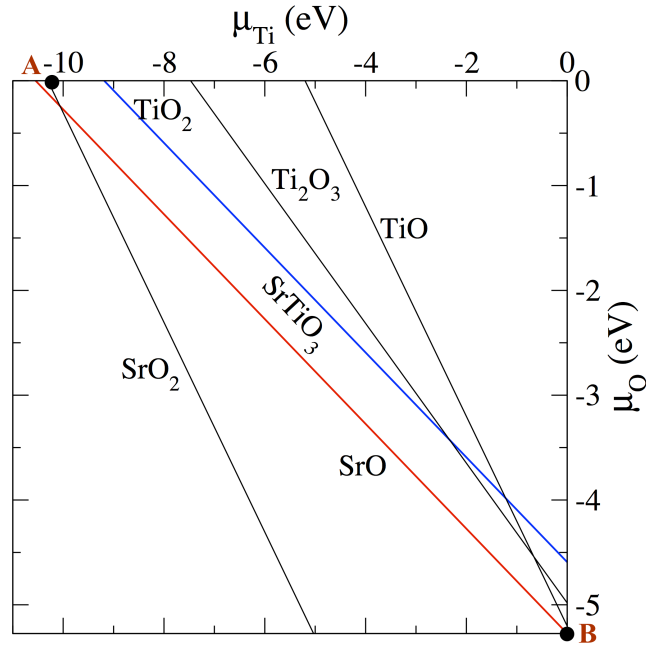


Figure 1 Chemical potentials conditions for stable growth of $SrTiO_3$ under thermodynamic equilibrium

5. Results

First of all, we report the calculated fundamental properties of the three perovskites. The calculated basic physical properties, i.e., (1) lattice constant (2) heat of formation and (3) band gap are shown in Table 1-3.

Table 1 Calculated lattice parameters of SrTiO₃, energy band gap (E_g) and formation enthalpy (ΔH_f) using functional PBE and HSE06, compared with the experimental values

	PBE	HSE06 ($\alpha = 0.28$)	Experiments
a (Å)	3.953	3.913	3.905
E_g (eV)			
- indirect	1.66	3.27	3.25
- direct	2.00	3.57	3.75
ΔH_f (eV)	-15.58	-16.20	-17.34

Table 2 Calculated lattice parameters of BaTiO₃, energy band gap (E_g) and formation enthalpy (ΔH_f) using functional PBE and HSE06, compared with the experimental values

	PBE	HSE06 ($\alpha = 0.30$)	Experiments
a (Å)	4.038	3.985	4.000
E_g (eV)			
- indirect	1.57	3.25	-
- direct	1.70	3.28	3.27
ΔH_f (eV)	-12.377	-15.90	-17.10

Table 3 Calculated lattice parameters of CaTiO₃, energy band gap (E_g) and formation enthalpy (ΔH_f) using functional PBE and HSE06, compared with the experimental values

	PBE	HSE06 ($\alpha = 0.30$)	Experiments
a (Å)	3.897	3.851	3.840
E_g (eV)			
- indirect	1.733	3.483	3.500
- direct	2.148	3.897	-
ΔH_f (eV)	-15.27	-15.90	-17.24

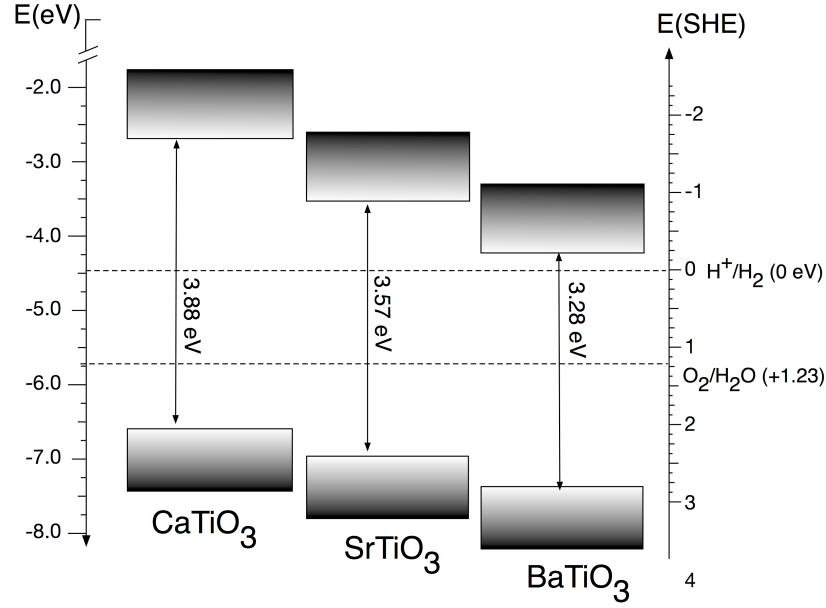


Figure 2 Calculated band offsets of CaTiO_3 , SrTiO_3 and BaTiO_3 .

We find that the values of lattice constant, band gap and heat of formation obtained by HSE are in good agreement with experimental values. In particular, by properly selecting the HF parameter, the calculated band gaps of all SrTiO_3 , BaTiO_3 and CaTiO_3 are in excellent agreement with experimental values. We expect the HSE is capable for not only reproducing the experimental band gaps but also improving electronic structure of the materials as well as formation energy of defects and dopants.

Band offsets of CaTiO_3 , SrTiO_3 and BaTiO_3 are calculated using the slab models in which the non-polar TiO_2 terminated surfaces were adopted. In the slab models, the supercell containing 48 atom with vacuum region more than 20 Å were used. The band edge positions referenced to the vacuum level are calculated by the following procedures. (1) the energy difference between the vacuum level (V_{vac}) and V_{ae} is calculated as $\Delta V_{slab} = V_{vac} - V_{ae}$, where V_{ae} is the average electrostatic potential in the bulk region of the slab. (2) the energy difference between the valence band edge position, E_{VB} and V_{ae} in the bulk unit cell is determined as $\Delta V_{bulk} = E_{VB} - V_{ae}$. We thus can estimate the valence band edge position as $E_{VB}(VAC) = \Delta V_{bulk} - \Delta V_{slab}$. The band offsets are shown in Fig.2. We find that the valence band edge position of the three perovskites are lower than the $\text{O}_2/\text{H}_2\text{O}$ oxidation potential and the conduction band edge positions are higher than H^+/H_2 reduction potential of water. The conduction band edge (E_{cbe}) and valence band edge (E_{vbe}) positions are in the order of $E(\text{CaTiO}_3) > E(\text{SrTiO}_3) > E(\text{BaTiO}_3)$.

Next, we address in detail the energetics and optical properties of selected N impurities in SrTiO_3 , which are (1) substitutional N at O site (N_O) (2) $\text{N}_O\text{-H}_i$ complex, in which hydrogen binds with N_O (3) $(\text{N}_2)_{2O}$ complex and (4) $(\text{NO}_2)_{2O}$ complex. Figure 3 shows the local atomic structures for N impurities in SrTiO_3 investigated in this project. The calculated formation energies for N_O , $(\text{NO})_O$, $(\text{NO}_2)_{2O}$, $(\text{N}_2)_O$ and $(\text{N}_2)_{2O}$ for the O-poor, intermediate (experimental), and O-rich conditions are shown

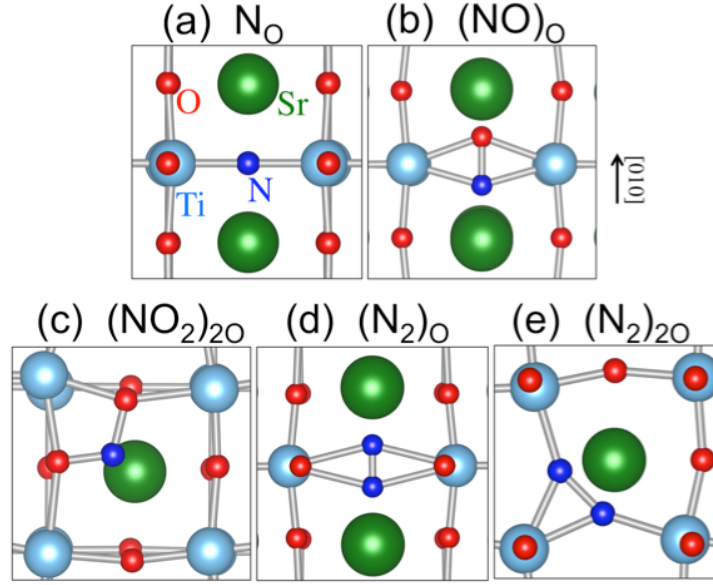


Figure 3 Local atomic structures of N impurities in SrTiO_3 : (a) N_O (b) $(\text{NO})_\text{O}$ (c) $(\text{NO}_2)_{2\text{O}}$ (d) $(\text{N}_2)_\text{O}$ and (e) $(\text{N}_2)_{2\text{O}}$

in Fig. 4. The formation energies for other conditions can be determined using appropriate values for the oxygen and nitrogen chemical potentials. Our calculated formation energies indicate that N_O is the prevalent defect for Fermi-level values near the conduction band for all conditions considered. N_O is expected to behave as an acceptor in SrTiO_3 , since N has one valence electron less than O, and can be stable in either the neutral (N_O^0) and negative charge states (N_O^-), which is the most energetically favorable defect for Fermi-level values near the conduction-band minimum. This conclusion remains valid for all values of O chemical potential between O-rich and O-poor. The thermodynamic transition level ($0/-$) is located at 1.51 eV above the VBM, indicating that N_O is a deep acceptor. This result is similar to the behavior of N_O in ZnO ³⁸ and TiO_2 ²⁸, and indicates that N_O cannot lead to p -type conductivity in SrTiO_3 .

The optical properties of N_O center are determined through the configuration coordinate diagram as shown in Fig. 3(a). The optical transitions associated with N_O occur through the process $\text{N}_\text{O}^- + h\nu \rightarrow \text{N}_\text{O}^0 + e^-$ in which N_O^- absorb a photon, converting to N_O^0 with an electron in the conduction band. The absorption energy was obtained by calculating the difference of formation energy between N_O^0 in N_O^- lattice geometry and N_O^- for E_F at the conduction band, and corresponds to the N_O -related absorption peak. We find that N_O leads to sub-band gap optical absorption peak centered at 2.46 eV, in which an electron is excited from the fully occupied states of N_O^- (Fig. 3(b)) to the conduction band. Our calculated absorption energy of 2.46 eV is in good agreement with the experimental observations, in which the absorption edge is reported to occur at about 500 nm (~ 2.48 eV).^{9,10} The calculated emission energy, representing a recombination of an electron in the conduction band with the hole in N_O^0 , i.e., $\text{N}_\text{O}^0 + e^- \rightarrow \text{N}_\text{O}^- + h\nu$, is 0.97 eV. This large difference between absorption and emission energy reflects a large Stokes shift, originating

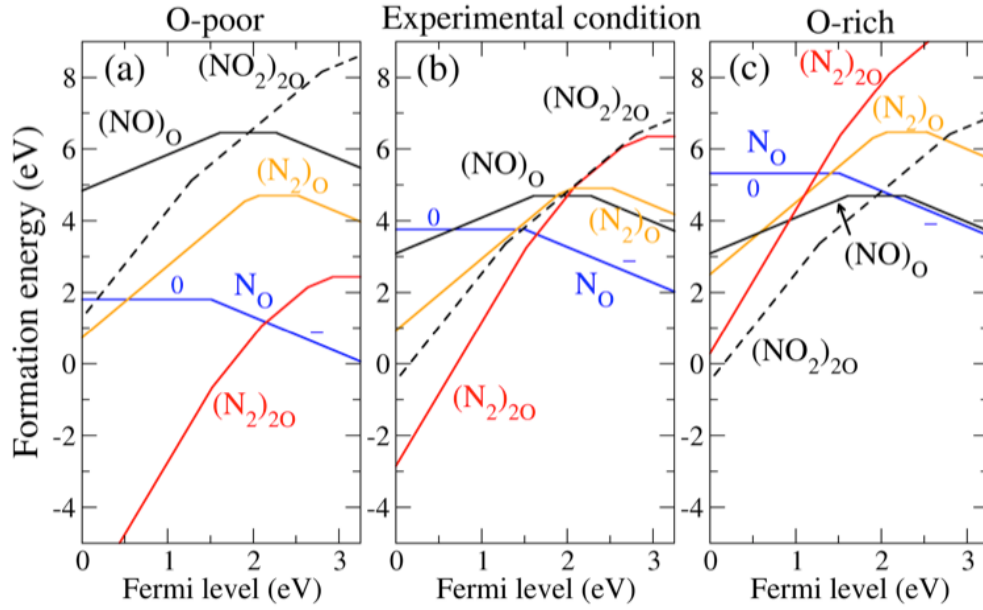


Figure 4 Formation energies of N-related defects as a function of Fermi level ranging from 0 to calculated band gap of 3.27 eV under (a) O-poor, (b) experimental and (c) O-rich growth conditions. The slopes of the line indicate the charge states of the defects.

from very different local atomic relaxations associated with N_O^0 and N_O^- . We find the Ti atoms surrounding N_O^0 relax outward by 1.53% with respect to equilibrium Ti-O bond length, while the Ti atoms surrounding N_O^- relax inward by 4.20 %. This large difference of local atomic relaxations also indicates that the absorption and emission peaks are quite broad. We also consider the transition through the process $N_O^0 + h\nu \rightarrow N_O^- + h^+$ in which an electron is transferred to N_O^0 , converting it into N_O^- with a hole in the valence band. The absorption energy can be calculated by constructing the configuration coordinate diagram in the same way, as shown in Fig. 3(a), which yields a value of 2.28 eV, slightly less than the absorption energy associated with the conduction band electron exchange. This value is in good agreement with a recent experimental observation in which the optical band gap of N-bombarded SrTiO_3 was reported to be 2.31 eV.¹⁷ In these experiments, it is likely that the Fermi level is pinned near the (0/−) transition level of N_O , leading to non-negligible concentrations of N_O^0 . Both processes lead to the visible-light absorption, albeit, the process centered on N_O^- yields slightly higher absorption energy than the process centered on N_O^0 does. In *n*-type SrTiO_3 , however, the process involving excitation of N_O^- is dominant and likely to contribute to photocatalysis processes, where an electron is excited to the conduction band.

Since hydrogen is an ubiquitous impurity and has been reported to play important role in the electrical properties of many oxides, it is worthwhile to consider the interactions between hydrogen and N in SrTiO_3 . First, we find that interstitial H (H_i) prefers to bind with host O without introducing any state in the band gap. It is exclusively stable in 1+ charge state (H_i^+), acting as a shallow donor. Our calculated result for H_i is in good agreement with the recent calculations based on the

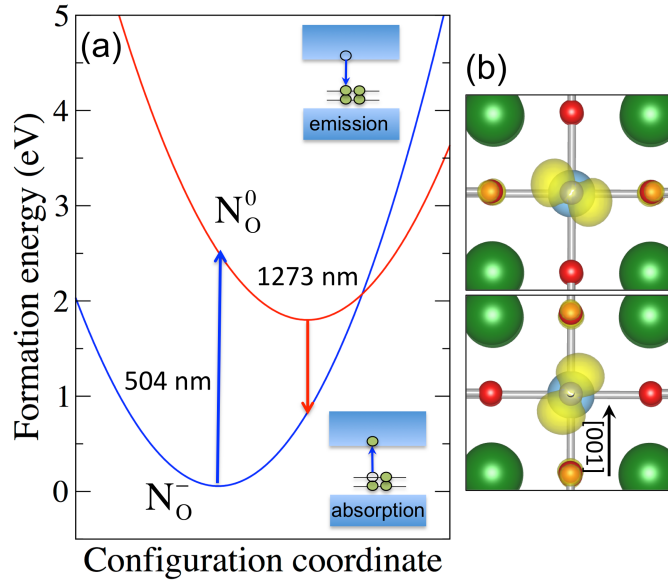


Figure 5 (a) Configuration coordinate diagram for N_O . The formation energies correspond to the similar condition in Fig. 2(a), and for E_F at the conduction-band minimum. (b) Charge distribution of N_O 2p states associated with the optical transition.

HSE06 screened hybrid-functional.⁴¹ The shallow donor behavior of H_i has been also reported in other oxide semiconductors. In addition, the migration barrier for H_i has been reported to be as low as 0.25 eV, indicating that it is highly mobile even at very low temperatures, unless it is trapped by other defects.⁴² We expect that H_i^+ can be trapped by N_O acceptors through Coulombic attraction. Figure 4(a) shows the calculated formation energies of N_O - H_i complex, H_i and N_O in $SrTiO_3$ under O-poor condition. We find that N_O - H_i occurs in 1+ and neutral charge states with the transition level (+/0) located at 1.23 eV above the VBM. This behavior of N_O - H_i in $SrTiO_3$ contrasts to that reported in TiO_2 in which N_O - H_i is only stable in the neutral charge state. In TiO_2 , H completely passivates the localized state of N_O^- that appears in the band gap, whereas in $SrTiO_3$ H partially passivates one of the localized states of N_O^- , leaving another N-related state in the band gap. Figure 5 illustrates the schematic diagram of N_O 2p and H_i s hybridization in TiO_2 and $SrTiO_3$. In TiO_2 , two electrons from N_O^- 2p occupy the bonding state and lie deep in the valence band, leaving the empty antibonding state resonant in the conduction band (Fig. 5(a)). Therefore, the localized gap state is absent and N_O - H_i can only be stable in the neutral charge state. In $SrTiO_3$, N_O^- induces two nearly-degenerated states, fully occupied by four electrons. This is a result of the difference in coordination number between TiO_2 and $SrTiO_3$; in TiO_2 N is threefold coordinated, while in $SrTiO_3$ N is twofold coordinated. Thus, two non-bonding states are present in the band gap in the case of $SrTiO_3$ while only one non-bonding state is present in the case of TiO_2 . While one of the two occupied state participates in N_O 2p and H_i s hybridization in $SrTiO_3$, another state does not and resides in the band gap (Fig. 5(b)). An electron can be removed from this state, resulting in $(N_O - H_i)^+$. We also consider the optical transition associated with the process $(N_O - H_i)^0 + h\nu \rightarrow (N_O - H_i)^+ + e^-$, in

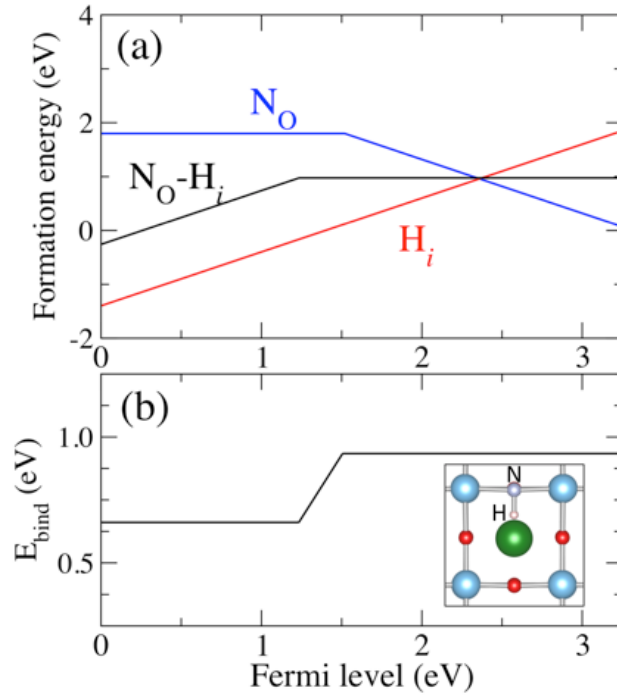


Figure 6 (a) Formation energies of N_O and H_i and N_O-H_i complex under the O-poor condition and (b) calculated binding energy of N_O-H_i as a function of Fermi level (see more details in the text). Inset shows the local atomic structure of N_O-H_i .

which an electron is excited from $(N_O - H_i)^0$ to the conduction band. The calculated absorption energy is 2.76 eV, higher than the absorption energy associated with N_O . This absorption energy is in good agreement with the experimental observations in N-doped SrTiO_3 samples that either highly contain hydrogen¹⁶ or used NH_3 as nitridizing source.⁴³

We also calculated the binding energy of the N_O-H_i complex, defined as:

$$E_b[(N_O - H_i)^q] = E^f[N_O^{q'}] + E^f[H_i^+] - E^f[(N_O - H_i)^q] \quad (1.2)$$

where $E^f[(N_O - H_i)^q]$ is the formation energy of the complex in charge state q ($q = 0, +$). $E^f[N_O^{q'}]$ is the formation energy of N_O in charge state q' ($q' = 0, -$). The calculated binding energy as a function of Fermi level is shown in Fig 4(b). The binding energy for $(N_O - H_i)^0$ is 0.94 eV, higher than that in TiO_2 (0.58 eV in rutile and 0.49 eV in anatase).²⁸ However, it is only 0.66 eV for $(N_O - H_i)^+$, when the Fermi level moves toward the valence band. Note that the binding energies remain unchanged for higher O chemical potentials. To address the stability of the complex, we estimated its dissociation energy, given by $E_b[(N_O - H_i)^0] + E_m(H_i^+)$, to be 1.2 eV, where $E_m(H_i^+)$ is the calculated migration barrier of interstitial hydrogen of 0.25 eV.⁴² $(N_O - H_i)^0$ is thus expected to be stable at temperatures of up to ~465 K. Our results indicate that the presence of H does not

completely reverses the visible light-absorption capability of N-doped SrTiO₃, instead it results in blueshifted absorption edge.

We also investigated the interaction between the two nearby substitutional N on O sites (N_O-N_O). We find that, through large lattice relaxations, the two N_O are coupled and spontaneously combine into a configuration of N₂ split-interstitial. This complex is denoted as (N₂)_{2O} and shown in Fig. 1(e). Recently, the coupling of two N_O in TiO₂⁴⁰ and SrTiO₃²⁶ were studied, however, the energetics of (N₂)_{2O} in charge states other than neutral and under different growth conditions were not considered, and the optical absorption was determined based on calculating absorption coefficient using dielectric tensors. (N₂)_{2O} in neutral charge state introduces two fully occupied states in the band gap. These electrons can be removed when the Fermi level moves toward the valence band. We thus find that (N₂)_{2O} can be stable in 4+, 3+, 2+, 1+ and neutral charge states with the transition levels (4+/3+), (3+/2+), (2+/+) and (+/0) at 1.52 eV, 2.09 eV, 2.64 eV and 2.93 eV above the VBM, respectively. Since substituting two O atoms are involved in the creation of (N₂)_{2O}, under the O-poor conditions (N₂)_{2O} has lower formation energy than (N₂)_O for all Fermi-level positions in the band gap. In addition, we examine the relative stability of (N₂)_{2O} complex with respect to two isolated N_O by calculating the binding energy defined as $E_b = 2E^f[\text{N}_\text{O}^0] - E^f[(\text{N}_2)_{2\text{O}}^0]$. A positive value of binding energy means that the neutral (N₂)_O is lower in energy than the isolated neutral N_O. Our calculated binding energy for (N₂)_O in SrTiO₃ is 1.17 eV, slightly smaller than the value reported in Ref.²⁶. To examine the optical transitions associated with (N₂)_{2O}, we considered processes involving electron transfer from the valence band to the defect state and from the defect state to the conduction band, i.e., (1) $(\text{N}_2)_{2\text{O}}^{3+} + h\nu \rightarrow (\text{N}_2)_{2\text{O}}^{2+} + h^+$, in which an electron is excited from the valence band into (N₂)_{2O}³⁺, leaving a hole in the valence band; (2) $(\text{N}_2)_{2\text{O}}^{3+} + h\nu \rightarrow (\text{N}_2)_{2\text{O}}^{4+} + e^-$, in which an electron is excited from (N₂)_{2O}³⁺ to the conduction band; (3) $(\text{N}_2)_{2\text{O}}^{4+} + h\nu \rightarrow (\text{N}_2)_{2\text{O}}^{3+} + h^+$, in which an electron is excited from the valence band into (N₂)_{2O}⁴⁺, leaving a hole. These processes yield the absorption energies of 2.77 eV, 2.61 eV and 2.52 eV, respectively, which fall into the visible-light region. Figure 2 shows that (N₂)_{2O} and N_O are dominant defects under O-poor and experimental conditions. At Fermi level about 2.15 and 1.63 eV above the VBM, which correspond to the intersections of the two formation energy lines for N_O and (N₂)_{2O}, the concentrations of (N₂)_{2O} and N_O are the same. This means that N_O and (N₂)_{2O} can comparably contribute to the light absorption in visible range in SrTiO₃ samples with Fermi-level positions near these values. Note that the formation energy of (N₂)_{2O} will decrease as twice as that of N_O when N chemical potential is raised. Therefore, in case of high-N doping, (N₂)_{2O} could become the dominant defect in a wider range of Fermi level (see Fig. S1).³⁹ We thus cannot exclude that (N₂)_{2O} can serve as a source of visible-light absorption in N-doped SrTiO₃. In addition, Figure 2 shows that (N₂)_{2O} which is a quadruple donor can be compensating center for N_O acceptor under O-poor and experimental conditions. This is because, the Fermi level will be pinned at about the intersections of the two formation energy lines for predominant N-related defects: N_O (acceptor) and (N₂)_{2O} (donor), at which a charge neutrality of the system is nearly satisfied among negatively charged N_O and positively ionized (N₂)_{2O}. Note that the free electron and

hole carriers were neglected in determining the pinned Fermi level because of the wide band gap of SrTiO₃. These pinned Fermi levels, which locate in the middle of the band gap far away from the VBM, indicate that hole carrier concentration is extremely low. Combined our results for N_O, which is a deep acceptor, and (N₂)_{2O}, which acts as active compensating center, we thus believe that N-doped SrTiO₃ cannot become *p*-type under these conditions.

In addition to split interstitial configuration, we find that N can bind with two nearby host O atoms, forming NO₂-like configuration (NO₂)_{2O} (Fig. 1(c)), which is energetically stable in 1+, 2+ and 3+ charge states. Under O-rich condition, (NO₂)_{2O} has relatively low formation energy for Fermi-level positions in the lower half of the band gap (Fig. 2(c)), indicating that it could exist with a significant concentration in SrTiO₃ that is grown under high oxygen partial pressures and Fermi level positions below ~1.9 eV with respect to the VBM. Optical transitions of (NO₂)_{2O} are considered to occur via the process (NO₂)_{2O}²⁺ + *hν* → (NO₂)_{2O}³⁺ + *e*⁻, in which an electron is excited from (NO₂)_{2O}²⁺ to the conduction band and the process (NO₂)_{2O}³⁺ + *hν* → (NO₂)_{2O}²⁺ + *h*⁺, in which an electron is excited from the valence band to (NO₂)_{2O}³⁺. These processes give absorption energies of 2.80 eV and 2.19 eV, respectively. It is thus possible that (NO₂)_{2O} contributes to the optical absorption in the visible region in some SrTiO₃ samples.

Finally, the optical transitions associated with N_O in CaTiO₃ and BaTiO₃ were also examined. We find that N_O leads to sub-band gap optical transitions at 3.10 for CaTiO₃, 2.23 for SrTiO₃, and 2.15 eV for BaTiO₃. The near ultraviolet absorption of N_O in CaTiO₃ indicates that the N_O levels are reasonably close to the valence band maximum compared to those in SrTiO₃ and BaTiO₃ where the photon absorption is in the visible-light region.

6. Conclusion and Discussion

In summary, based on hybrid-density functional calculations, we have investigated the thermodynamic stability and the effects of N impurities on optical absorption in SrTiO₃. We find that substitutional N_O is a deep acceptor and energetically favorable over other N impurity configurations in *n*-type SrTiO₃. Our calculations show that N_O gives rise to optical absorption in the visible region, consistent with the experimental observations. We also find that hydrogen can bind with N_O. In contrast to TiO₂, formation of N_O-H_i complex does not completely reverses the N_O-induced visible-light absorption, yet it leads to a blueshift in the absorption edge. Our results indicate that N_O-H_i can explain the observed optical absorption in the samples prepared with highly-H contained nitridizing sources. Higher binding energy of N_O-H_i in SrTiO₃ compared to that in TiO₂ indicates that thermal annealing at higher temperatures is needed to remove H, restoring the optical properties of N_O. Our results suggest that the other possible N configurations also contribute to optical absorption in the visible range. In addition, we find that (N₂)_{2O} acts as active compensating donor for N_O acceptor; thus it is very unlikely to use N for *p*-type doping. In addition, we investigate optical absorption associated with N_O in CaTiO₃ and BaTiO₃. The near ultraviolet absorption is found in CaTiO₃ whereas visible-light absorption is found in BaTiO₃ quite similar with SrTiO₃ case.

7. Output (Acknowledge the Thailand Research Fund)

7.1 International Journal Publication

(1) Pakpoom Reunchan, Naoto Umezawa, Anderson Janotti, Jiraroj T-Thienprasert, Sukit Limpijumnong. Energetics and optical properties of nitrogen impurities in SrTiO_3 from hybrid density-functional calculations. *Physical Review B* **95**, 205204 (2017) [included in Appendix].

7.2 International conference

(1) Pakpoom Reunchan, Naoto Umezawa, Anderson Janotti, Jiraroj T-Thienprasert, Sukit Limpijumnong. Energetics and optical properties of nitrogen impurities in SrTiO_3 from hybrid density-functional calculations. 29th International Conference on Defects in Semiconductors, July 31 – August 4, 2017, Matsue, Shimane prefecture, Japan. [Poster presentation].