

# Theoretical investigations on controlling the properties of semiconductor photocatalysts by modifying structural factors

その他のタイトル	半導体光触媒の構造的要因を利用した物性制御に関する理論的研究
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## 論文の内容の要旨

論文題目 Theoretical investigations on controlling the properties of semiconductor photocatalysts by modifying structural factors  
(半導体光触媒の構造的要因を利用した物性制御に関する理論的研究)

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### **Chapter 1. General Introduction**

Photocatalytic or photoelectrochemical water splitting have been getting wide attention due to their ability to produce hydrogen from a renewable energy source. Most of the photocatalysts and photoelectrodes consist of semiconductors, and their activities are strongly related to their fundamental properties.

Recently, a large number of mixed ion compounds such as oxynitrides and solid solutions have been reported as promising candidates for photocatalysts or photoelectrode materials. The advantageous feature of such compounds is the broad range of controllability of their fundamental properties due to the wide variety of their structural features such as atomic arrangements, chemical compositions, and defect structures. However, there also exists a huge barrier to understand the structural and the electronic features of such mixed ion compounds, since their complex structural features make it a challenging task to measure them microscopically or to relate them to the fundamental properties of the compounds.

Thus, in this thesis, I investigated the structural and the electronic features of such mixed ion compounds by means of first-principle calculations. Furthermore, I aimed to relate their structural factors to their fundamental properties in order to provide the guidelines to control their properties and to enhance their photocatalytic or photoelectrochemical activities for water splitting.

### **Chapter 2. First Principle Approaches to the Electronic Structure of Solids**

In chapter 2, I presented the theoretical framework to calculate the electronic structures of solids from first principle. In particular, I focused on how the electronic structures of materials are obtained from the geometry of their constituent atomic nuclei, and then traced the development of the theories basing on the fundamental quantum mechanics. Additionally, I explained the approximate methods used in the calculations of the electronic structures of many body systems such as solids, and showed how they influence the description of the electronic structures.

### **Chapter 3. Effects of Anion Ordering in Perovskite Oxynitride: A Demonstration on CaTaO<sub>2</sub>N**

In chapter 3, I focused on the specific anionic arrangements of O/N (= anion ordering) in perovskite oxynitrides, a group of compounds which have been promising candidates for visible-light responsive photocatalysts. Here, I investigated the correlation between the anion ordering of CaTaO<sub>2</sub>N, a major example of a perovskite oxynitride that had achieved overall water splitting under visible light, and its photocatalyst related properties such as bandgaps, carrier effective masses, and band edge positions, in order to obtain the guidelines to modify the properties of CaTaO<sub>2</sub>N by controlling its anion ordering.

As a result, it was revealed that the valence band structures of CaTaO<sub>2</sub>N varies as a function of its anion ordering. In particular, the positions of the valence band maximum (VBM) of three-dimensional anion orderings were found to be more positive than those of two-dimensional ones by up to 0.5 eV. Thus, it is expected that the oxygen evolution ability of CaTaO<sub>2</sub>N will be improved by modifying its anion ordering into a three-dimensional fashion.

By analyzing the electronic structures, it was also found that the difference in valence band structure among the anion orderings stems from the different orbital overlap between the Ta 5d and N 2p bands (d-p $\pi$  interactions). In two-dimensional anion orderings the two bands cannot overlap due to their symmetry mismatch. On the other hand, the symmetry of N 2p bands are lowered in three-dimensional anion orderings, and thus the overlap with Ta 5d bands becomes allowed and a net stabilization of the valence band was induced.

### **Chapter 4. Effects of Octahedral-Tilting and Crystal Polymorphism: A Demonstration on MgTaO<sub>2</sub>N**

In chapter 4, I discussed the applicability of MgTaO<sub>2</sub>N, a theoretically predicted novel oxynitride photocatalyst, by tackling the remaining issue regarding the effect of its octahedral-tiltings and crystal polymorphism that had not been considered in the previous studies using computational screening. Here, I estimated the fundamental properties of MgTaO<sub>2</sub>N in perovskite polymorph using structural models where the octahedral-tiltings had been taken into account, and investigated the correlation between the octahedral-tiltings and the photocatalyst related properties. Besides, I also calculated the properties of MgTaO<sub>2</sub>N in ilmenite polymorph to estimate its applicability as a water splitting photocatalyst.

As a result, it was found that MgTaO<sub>2</sub>N in perovskite polymorph has suitable band edge positions for overall water splitting, though its bandgap is larger than the energy of visible-light and thus necessitates a sort of further modification. On the other hand, the bandgap and the band edge positions of MgTaO<sub>2</sub>N in ilmenite polymorph were found to be hardly suitable as a water splitting photocatalyst.

The results also showed the strong correlation between the octahedral-tiltings and the conduction band structures in perovskites. In particular, it was revealed that the electron effective mass increases and the positions of the conduction band minimum (CBM) rises with increasing octahedral-tiltings. According to such insights, in the perovskite-type MgTaO<sub>2</sub>N material design for photocatalytic application, suppressing its octahedral-tiltings will be highly desirable in order to lower the CBM positions and subsequently reduce its bandgaps while keeping the suitable positions of its band edges.

### **Chapter 5. Composition Dependence of Oxynitride Solid Solution: A Demonstration on LaMg<sub>x</sub>Ta<sub>1-x</sub>O<sub>1+3x</sub>N<sub>2-3x</sub>**

In chapter 5, I focused on LaMg<sub>x</sub>Ta<sub>1-x</sub>O<sub>1+3x</sub>N<sub>2-3x</sub> ( $0 \leq x \leq 2/3$ ), a solid solution photocatalyst that had achieved overall water splitting under visible light. Here, I investigated the dependence of its photocatalyst related properties on its composition in order to reveal the factor that made the photocatalytic activity of LaMg<sub>x</sub>Ta<sub>1-x</sub>O<sub>1+3x</sub>N<sub>2-3x</sub> reach the maximum at  $x = 1/3$ .

As a result, it was found that LaMg<sub>x</sub>Ta<sub>1-x</sub>O<sub>1+3x</sub>N<sub>2-3x</sub> balances two competing factors, a bandgap narrower than the energy of the visible light and band edge positions suitable for splitting water, at intermediate compositions. This is because, with increasing  $x$ , the contribution of O 2p in the valence band increases instead of the decrease in that of N 2p, and thus the position of VBM lowers and consequently the bandgap widens.

Additionally, it was also revealed that the band dispersion in the valence band increases at intermediate compositions due to the efficient hybridization between N 2p and O 2p. Besides, it was indicated that such hybridization between the two constituent orbitals prevents the hole localization on nitride ions, especially at  $x = 1/3$ , and thus suppresses the self-oxidation reaction ( $2\text{N}^{3-} + 6\text{h}^+ \rightarrow \text{N}_2$ ).

### **Chapter 6. Elucidation and Control of Defects in Solid Solution Photoelectrode: A Demonstration on (ZnSe)<sub>0.85</sub>(CuIn<sub>0.7</sub>Ga<sub>0.3</sub>Se<sub>2</sub>)<sub>0.15</sub>**

In chapter 6, I focused on (ZnSe)<sub>0.85</sub>(CuIn<sub>0.7</sub>Ga<sub>0.3</sub>Se<sub>2</sub>)<sub>0.15</sub>, a solid solution photocathode material consisting of p-type semiconductor. Here, I investigated the structures and the properties of the point defects in (ZnSe)<sub>0.85</sub>(CuIn<sub>0.7</sub>Ga<sub>0.3</sub>Se<sub>2</sub>)<sub>0.15</sub> in order to unravel the origin of the p-type characteristics of this material. I also estimated the dependence of the concentrations of such defects and the positive carriers on the external conditions, such as partial pressures, to obtain a guideline to enhance its photocathodic activities.

As a result, it was found that the dominant point defects in the solid solution, (ZnSe)<sub>0.85</sub>(CuIn<sub>0.7</sub>Ga<sub>0.3</sub>Se<sub>2</sub>)<sub>0.15</sub>, are the six antisites, Cu<sub>Zn</sub>, In<sub>Zn</sub>, Ga<sub>Zn</sub>, Zn<sub>Cu</sub>, Zn<sub>Ga</sub>, and Zn<sub>In</sub>.

Among these defects  $\text{In}_{\text{Zn}}$ ,  $\text{Ga}_{\text{Zn}}$ , and  $\text{Zn}_{\text{Cu}}$  work as donors and  $\text{Cu}_{\text{Zn}}$ ,  $\text{Zn}_{\text{In}}$ , and  $\text{Zn}_{\text{Ga}}$  work as acceptors, and thus the latter were presumed to be the origin of its p-type characteristics.

Additionally, it was also revealed that the p-type characteristics of  $(\text{ZnSe})_{0.85}(\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2)_{0.15}$  will be enhanced under Cu-rich condition, due to the enhanced formation of the dominant acceptor,  $\text{Cu}_{\text{Zn}}$ , and the suppressed formation of the dominant donor,  $\text{Zn}_{\text{Cu}}$ . Indeed, a similar trend had also been reported in previous experimental studies, where the enhanced photocurrent of this material was observed under Cu-rich conditions, and where the material showed n-type characteristics under Cu-poor conditions, indicating the high validity of the guidelines obtained in this research.

## **Chapter 7. Concluding Remarks**

In chapter 7, I summarized the research topics, results, and the conclusions reported in the previous chapters, and subsequently presented the concluding remarks based on the insights obtained through this thesis. Furthermore, a future outlook was provided in order that the next challenges to develop the photocatalytic research field may be presented for the researchers in the future generations.