# 論文 / 著書情報
# Article / Book Information

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# 論 文 要 旨

THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）


Solar energy is immensely attractive as a renewable energy source because of its abundance and the imminent exhaustion of fossil fuels. Solar cells are key devices for utilizing solar energy. Although various photoabsorber materials have been developed in the past several decades, photoabsorbers that achieve high power conversion efficiencies typically contain precious metals or toxic elements such as III–V compounds, $Cu(In,Ga)(S,Se)_2$, CdTe, and lead halide perovskites. Of the alternative photoabsorber materials thus far reported, ternary zinc nitrides are of particular interest because they can be manufactured entirely from earth-abundant and non-toxic elements and have suitable electrical and optical properties. The design and exploration of ternary zinc nitrides based on first-principles calculations have been accelerating in recent years, and previously unreported materials such as $CaZn_2N_2$ have been proposed theoretically and verified experimentally. However, unexplored chemical space of the ternary zinc nitrides remains. Further investigations are expected to identify more promising materials.

In this thesis, I focused on $AZn_2N_2$-type and $AZn_3N_3$-type ternary zinc nitrides and their crystal structures were determined using computational screenings based on first-principles calculations. In addition, I theoretically investigated their fundamental electronic and point-defect properties and experimentally verified the predicted crystal and electronic structures. The major results obtained in this study are as follows.

My computational screening for the crystal structures of $AZn_2N_2$ revealed that $SrZn_2N_2$ is stable whereas $BaZn_2N_2$ is metastable. $SrZn_2N_2$ takes an anti-$La_2O_3$-type crystal structure, which is the same as the crystal structure of $CaZn_2N_2$. My calculations showed that $SrZn_2N_2$ has a direct-type band structure with low electron and hole effective masses and shows strong optical absorption. Theoretical defect analysis indicates that the N vacancy generates defect levels at 0.19 and 0.44 eV above the valence band maximum. However, the N vacancy is unlikely to significantly affect the photovoltaic performance when the Fermi level is positioned at the mid-gap or *n*-type region by optimization of crystal growth conditions or extrinsic doping. The $SrZn_2N_2$ powder was synthesized by $NH_3$ nitridation of $SrZn_2$ alloy at 600℃. The band gap of $SrZn_2N_2$ was experimentally determined to be 1.6 eV, which is close to the theoretical value. $SrZn_2N_2$ is a promising material for single-junction solar cells because it has an optimal band gap and electrically benign point-defect properties and consists of earth-abundant elements.

Additionally, a systematic comparison of $CaZn_2N_2$, $SrZn_2N_2$, and $CaMg_2N_2$ was conducted. My integrated approach with chemical bonding analysis and defect energetics showed that, in $CaZn_2N_2$ and $SrZn_2N_2$, the Zn-3*d* states construct antibonding interactions with the N-2*p* states and push up the valence band maxima, resulting that the localized states induced by the cation vacancies are located near or in the valence bands. In contrast, the cation vacancies in $CaMg_2N_2$ generate deep defect levels due to no antibonding interaction near the valence band maximum. Among the ternary zinc nitrides, the defect levels of the Zn vacancy in $CaZn_2N_2$ are shallower than in $SrZn_2N_2$ because of the stronger antibonding interaction of the Zn-3*d* and N-2*p* states.

I also explored the crystal structures of previously unreported $ScZn_3N_3$ and $YZn_3N_3$. The predicted ground-state structures of $ScZn_3N_3$ and $YZn_3N_3$ are the $ScAl_3C_3$-type. The $YZn_3N_3$ phase is more stable than its competing phases while the $ScZn_3N_3$ phase is metastable. My calculations revealed that $YZn_3N_3$ has a direct-type band structure with a band gap of 1.8 eV and that its native defects are unlikely to make a significant impact on carrier lifetime thanks to the antibonding interaction of the Zn-3*d* and N-2*p* states as well as $CaZn_2N_2$ and $SrZn_2N_2$. I also grew $YZn_3N_3$ films on glass substrates by reactive co-sputtering and validated the theoretically predicted crystal structure. The experimentally determined band gap of 1.8 eV agrees well with the theoretical value. Given its appropriate band gap, low effective masses, high optical absorption, and good defect behavior, I propose $YZn_3N_3$ as a new candidate for top-cell materials in tandem solar cells.

The ternary zinc nitrides $SrZn_2N_2$ and $YZn_3N_3$ identified in this study are attractive candidates for solar absorbers. These materials are found to show strong optical absorption associated with their direct-type band structures and have optimal band gaps for single-cell and top-cell photoabsorbers, respectively. My theoretical calculations have also elucidated that the valence band maxima of $SrZn_2N_2$ and $YZn_3N_3$ include the antibonding interactions of the Zn-3*d* and N-2*p* states and the defect-induced acceptor levels in these materials tend to be shallow or buried in the valence bands thanks to the antibonding interactions. This defect behavior is suited to the active layers for solar energy conversion.


備考 ： 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。
Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1copy of 800 Words (English).