Exploring Zn-based Compounds for Visible Light Induced Photocatalysts

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The implications of climate change urge the need for efficient alternative energy sources such as H_2 gas. H_2 gas can be produced by reducing and oxidizing (splitting) of water; however, this process is thermodynamically unfavorable. Many catalysts already exist that can utilize UV light to assist in the splitting of water, but compounds that can utilize visible light, which have a band gap of less than 3.0eV, are still being developed. Mixed anion compounds, which often have small band gaps, have great potential to split water with visible light. A variety of oxynitrides with perovskite structure and their derivatives, which have octahedral coordination, have proved to be successful visible light induced photocatalysts. However, one of the most efficient visible light induced photocatalysts is ZnO-GaN, which has a wurzite crystal structure, with tetrahedral coordination. It is thought that Zn-based mixed anion compounds are promising catalysts due to the Zn-N bonds that raise the energy of the valence band. Unfortunately, it is harder to derive new materials from this solid solution due to the inflexibility in the wurzite structure for chemical substitutions. This research project focuses on the advancement of the knowledge surrounding visible light induced photocatalysts with tetrahedral coordination through synthesis of new Zn-based compounds. Inspired by $SrZnO_2$, synthesis of the new compound $Sr(Zn_{(1-x)}Ga_x)O_{(1-x)}N_x$ was used as a route to understand tetrahedral photocatalysts and mixed anion compounds as a whole.

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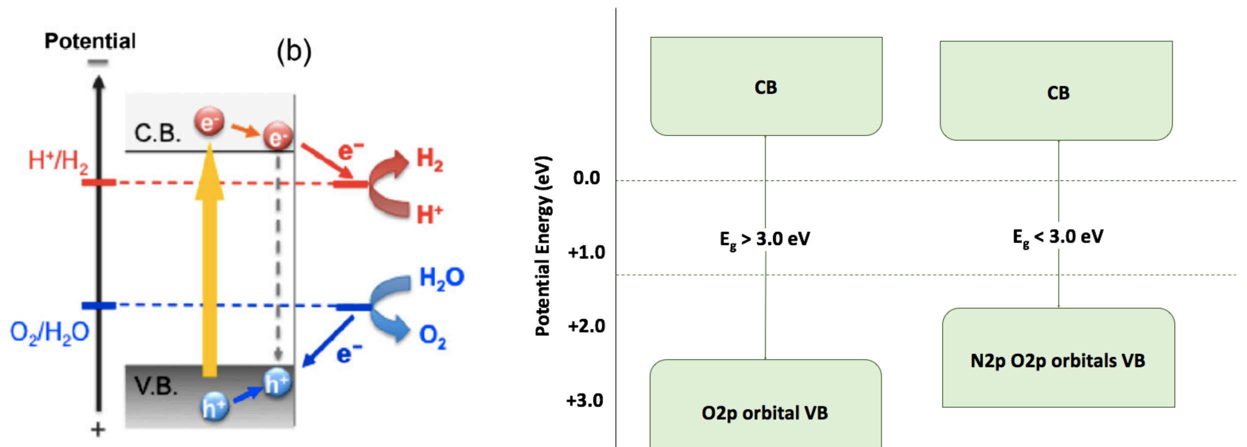
Objective

Understand how **oxynitride compounds** with **tetrahedral coordination** can be utilized as visible light induced photocatalysts.

Visible Light Photocatalysts

Climate change will not wait for science to catch up; **efficient alternative energy sources need to be developed.**

$H_2O + hv \rightarrow H_2 + ½ O_2$



- Catalysts that can utilize visible light (**b.g < 3.0 eV**) are essential for efficient H_2 production
- **Mixed oxyanion compounds** have small band gaps
- Current research focuses on **perovskite structure oxynitrides** (octahedral coordination)

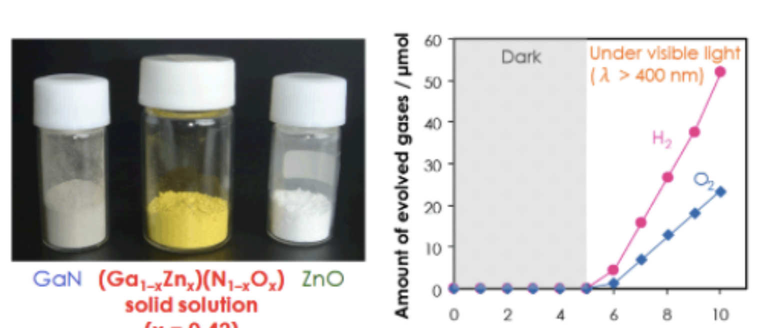
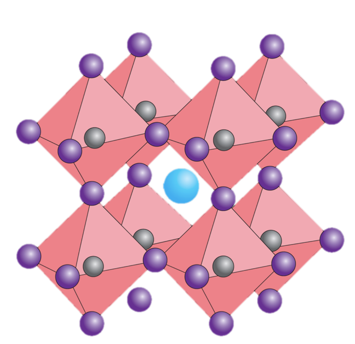
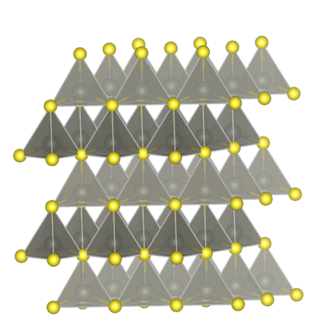


図3. 可視光で水を水素と酸素に直接分解する光触媒、窒化ガリウム－酸化亜鉛固溶体



Maeda, K *et al.* *JACS*, **2005**, 127 8289-8287

- **ZnO-GaN** has a suitable **band gap** and exhibits efficient photocatalytic activity
  - Zn-N bonds raise energy of valence band
  - **Wurzite structure** (tetrahedral coordination)

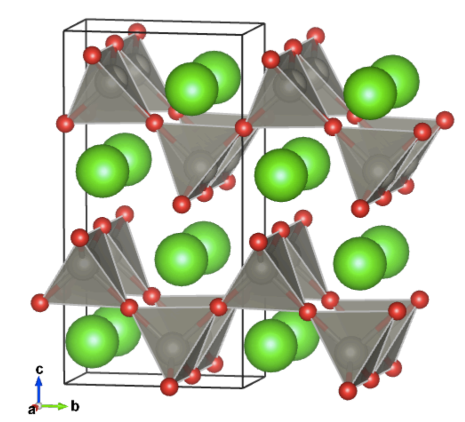


$Sr(Zn_{(1-x)}Ga_x)O_{(2-x)}N_x$ and **LaZnON** were investigated as potential visible light induced photocatalysts.

Theory and Synthesis Methodology

Thought Process for Constructing New Mixed Oxyanions

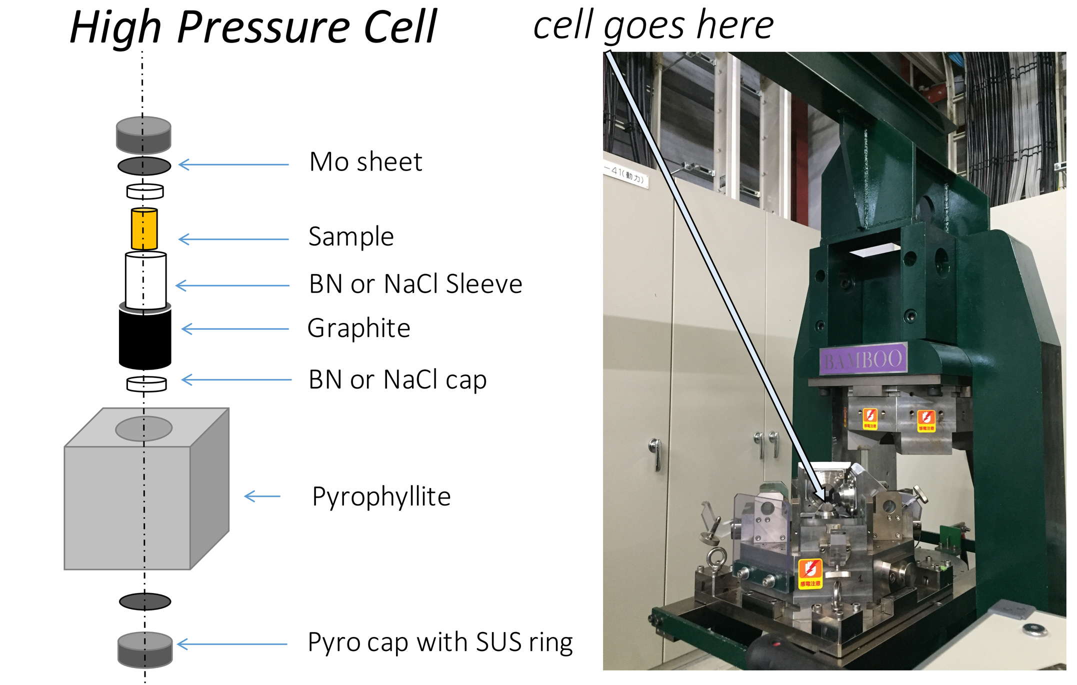
- Base structure
- Charge Neutrality
- Radius of substituted cation



$\overset{+2\ -2\ -2}{SrZnO_2} \rightarrow \overset{+2\ +2\ -2\ \ -3}{SrZnO_{(2-x)}N_x} \rightarrow \overset{+2\ \ +2\ \ \ +3\ \ -2\ \ -3}{Sr(Zn_{(1-x)}Ga_x)O_{(2-x)}N_x}$

NC = 0 | NC = - *x* | NC = 0

High Pressure Cell *cell goes here*



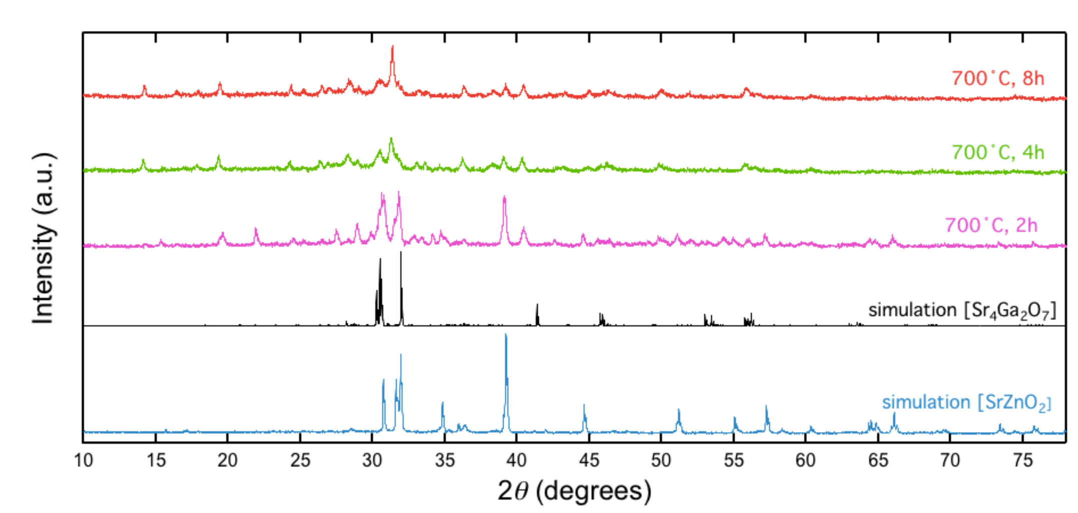
Results and Discussion

$Sr(Zn_{(1-x)}Ga_x)O_{(2-x)}N_x$

SrO + *(1-x)*ZnO + ½ *x*Ga_2O_3 *x = 0.1*

$Sr(OH)_2$ is formed

(x/3)$Sr_3Ga_2O_6$ + *(1-x)*$SrZnO_2$ + *(x/6)*Ga_2O_3 *x = 0.2*

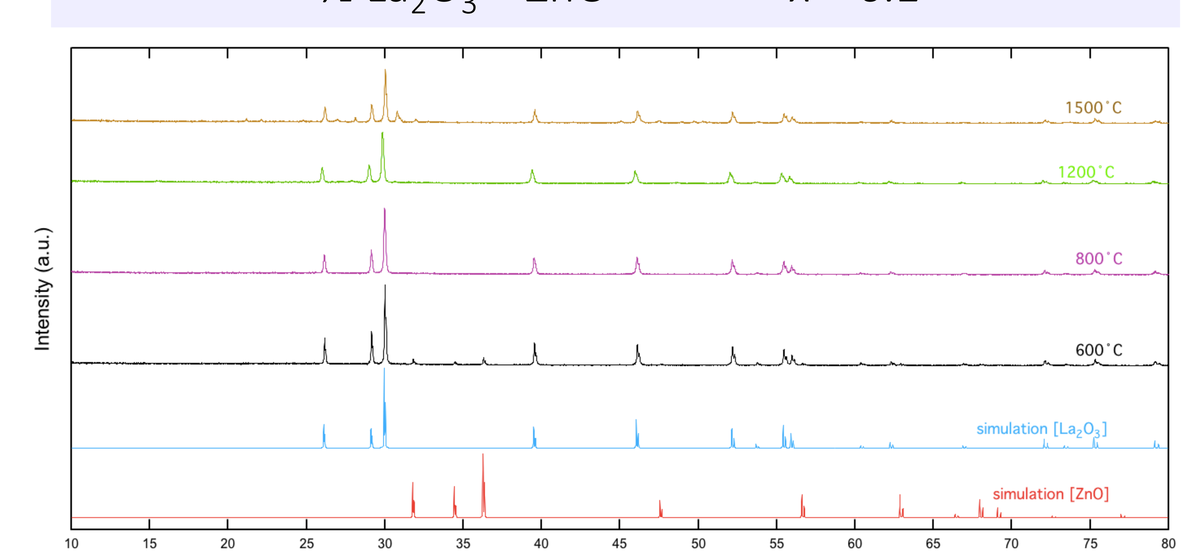


Attempted synthesis with NH_3 gas flow; unclear peaks formed.

- Ambiguous whether $Sr_4Ga_2O_7$ or $SrZnO_2$ was produced
- Lattice parameters did not change → no substitution

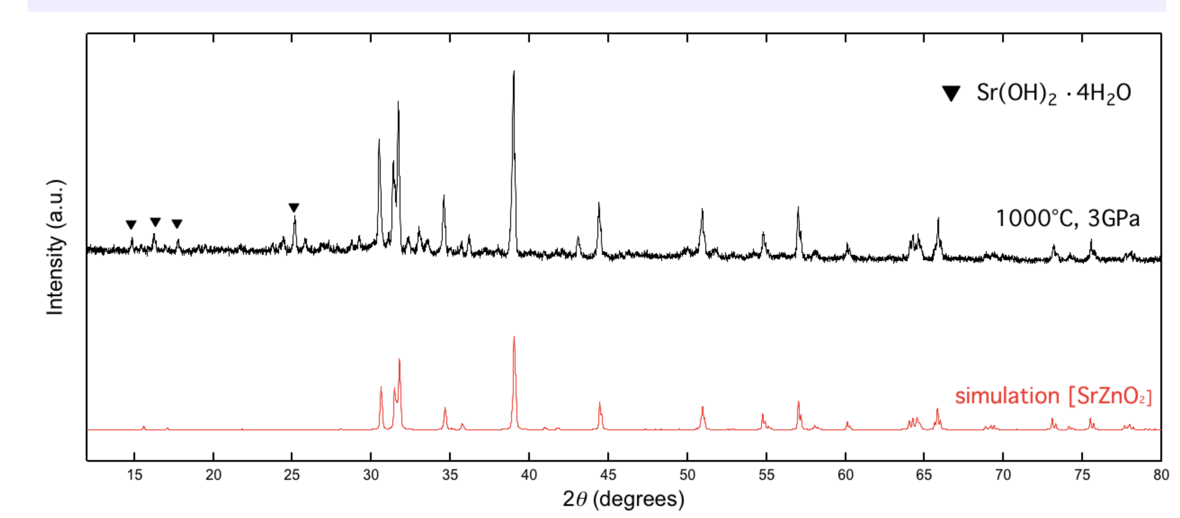
LaZnON

½ La_2O_3 + ZnO *x = 0.1*



NH_3 synthesis at two different temperatures; reaction did not occur.

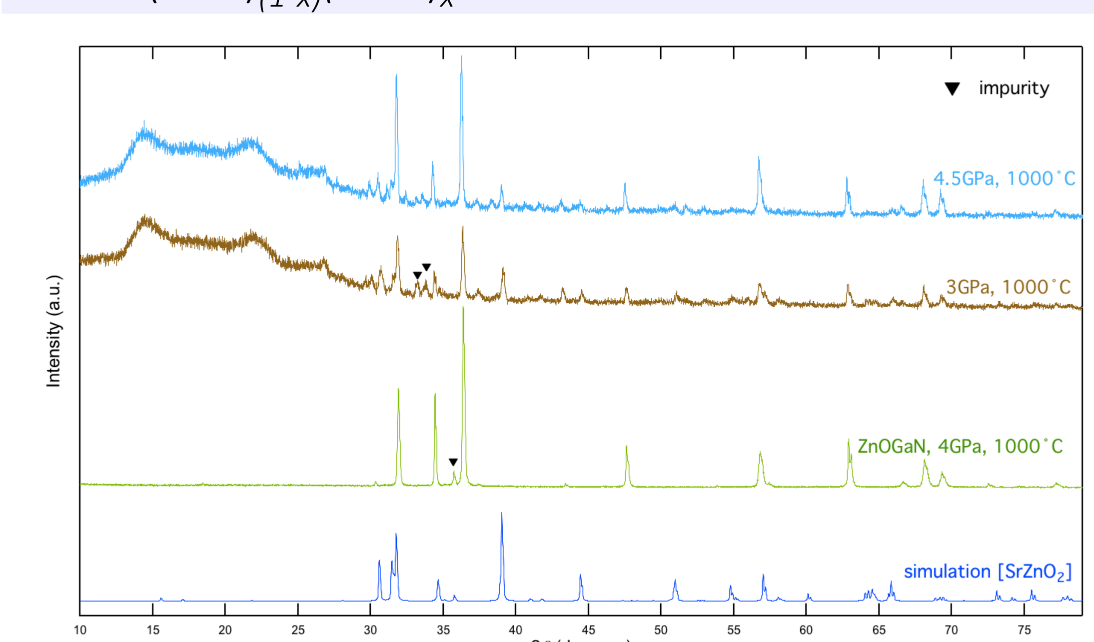
SrO + (*1-x*)ZnO + *x*GaN *x = 0.1*



High pressure synthesis; peaks did not shift.

Lattice parameters did not change → no substitution

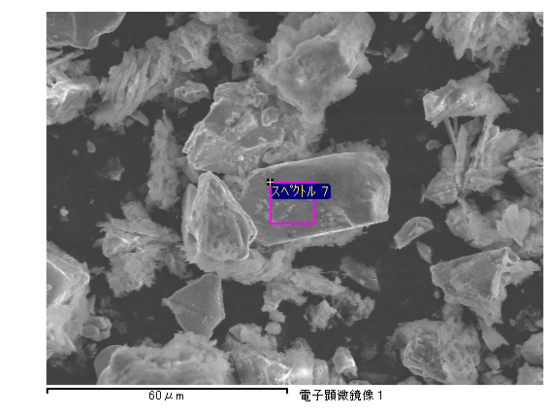
(*1-x*)ZnO + *x*GaN → $(ZnO)_{(1-x)}(GaN)_x$ *x = 0.25*
SrO + $(ZnO)_{(1-x)}(GaN)_x$



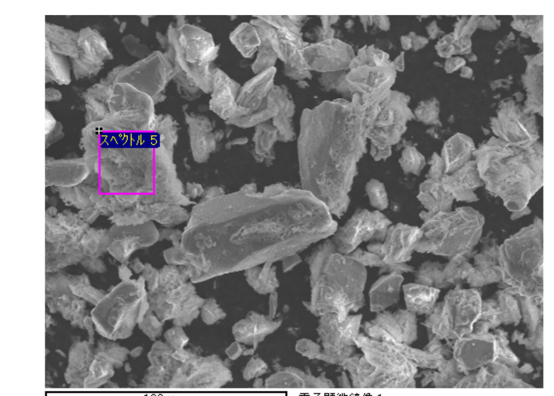
Mixed phases of ZnOGaN and $SrZnO_2$. No SrO peaks.

Comparing Lattice Parameters

	a (Å)	c (Å)
ZnO-GaN	3.2411	5.2112
3GPa, 900°C	3.2393	5.2128
4.5GPa, 1000°C	3.2404	5.2125

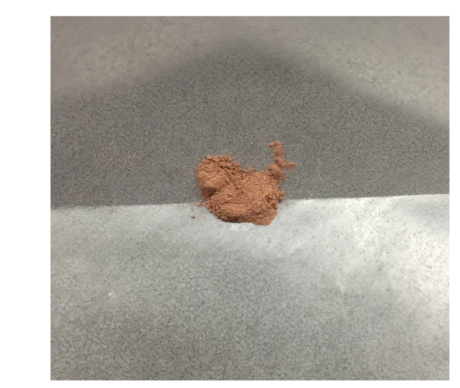


元素	質量濃度	原子数
	[%]	濃度[%]
N K	2.20	5.48
O K	27.56	60.06
Zn L	43.22	23.05
Ga L	6.49	3.25
Sr L	20.52	8.16
トータル	100.00	

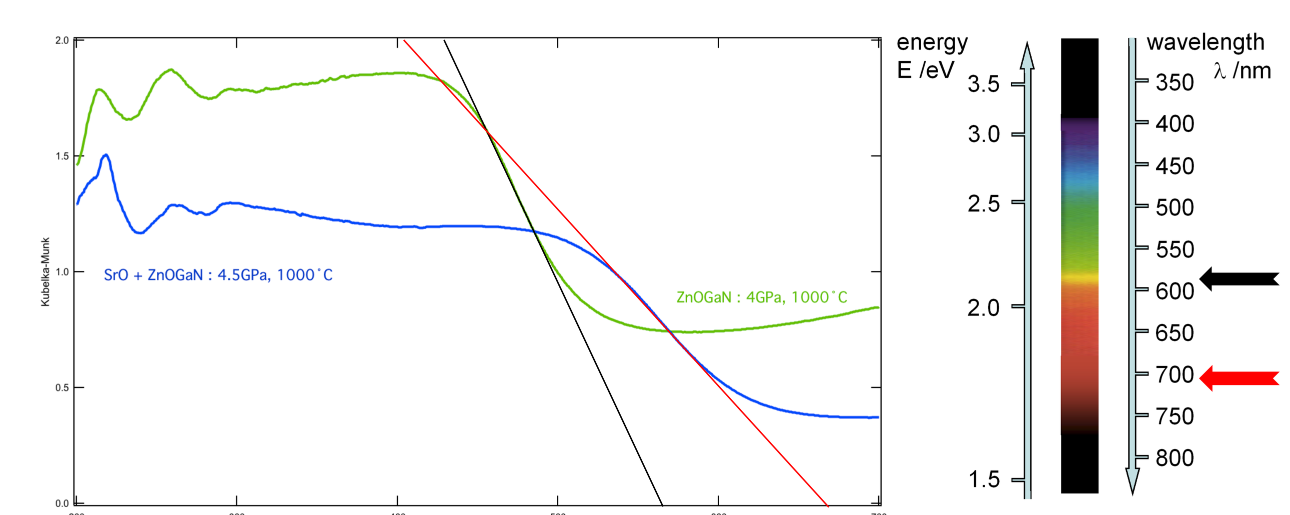


元素	質量濃度	原子数
	[%]	濃度[%]
N K	1.51	3.51
O K	35.31	71.62
Zn L	10.23	5.08
Ga L	1.90	0.88
Sr L	51.05	18.91
トータル	100.00	

- Rough crystals higher Sr content, smooth crystals lower Sr content
- **SrO is not present, but lattice parameters did not change**
- Dark green to rose pink



Sample after reaction (4.5 GPa, 1000°C).



Band gap of sample is smaller than ZnOGaN!

Future Work

High Pressure synthesis of ZnOGaN and SrO requires further investigation.

- Investigate the change in band gap
- Analyze the Sr phase present in the sample
- Understand reason behind drastic color change

Acknowledgements

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