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# A novel oxynitride photocatalyst system for water splitting :



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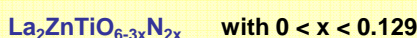
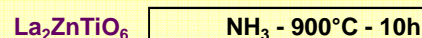
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The photocatalytic splitting of water under solar radiations is a challenging and promising domain of research to provide clean and renewable H<sub>2</sub> as an alternative energy resource. Current oxide photocatalysts (TiO<sub>2</sub>, ZnO, SrTiO<sub>3</sub>, NaTaO<sub>3</sub>...) are wide-gap semiconductors for which UV-light is necessary to produce electron-hole pairs by photoexcitation. However, the UV light represents only a small fraction (5%) of the solar spectrum. So far the (oxy)nitride approach become attractive for the efficient utilization of solar energy. A consequence of the anionic N<sup>3-</sup>/O<sup>2-</sup> substitution results in an increase of the covalent character which is illustrated by a shift of the absorption edge towards higher wavelength values (band gap < 3 eV). However other requirements have to be considered to synthesize an efficient visible-light-driven photocatalyst such as the mobility of the photogenerated charge carriers, the crystal structure or the chemical stability. Here, we have investigated the monoclinic perovskite-type oxynitride system La<sub>2</sub>Zn<sub>1-x</sub>Ti<sub>1+x</sub>(O,N)<sub>6</sub>.

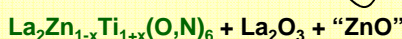
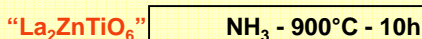
## Synthesis

**Citrate route 1000°C crystallized powders**



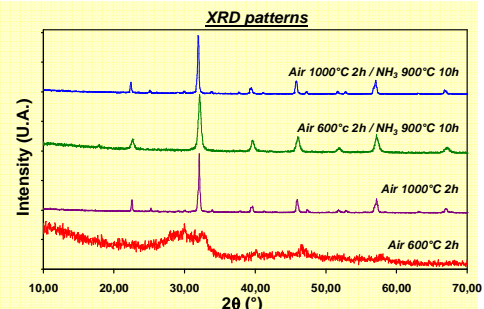
"La<sub>2</sub>ZnTiO<sub>6</sub>" - type structure - double perovskite

**Citrate route 600°C "poorly crystallized" powders**



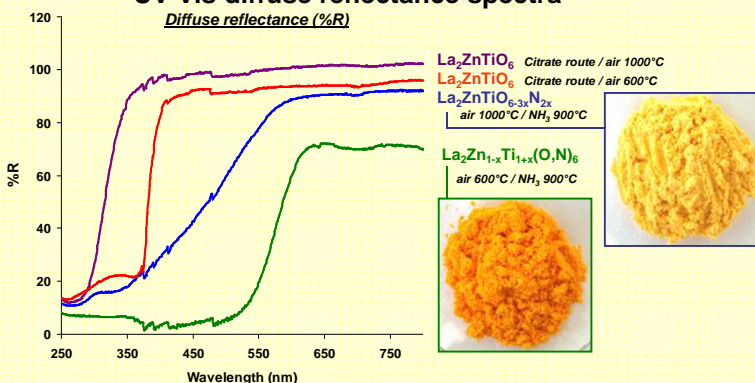
"LaTiO<sub>2</sub>N" - type structure - simple perovskite

Note: La<sub>2</sub>O<sub>3</sub> easily removed by washing with dilute HCl (0.1M)



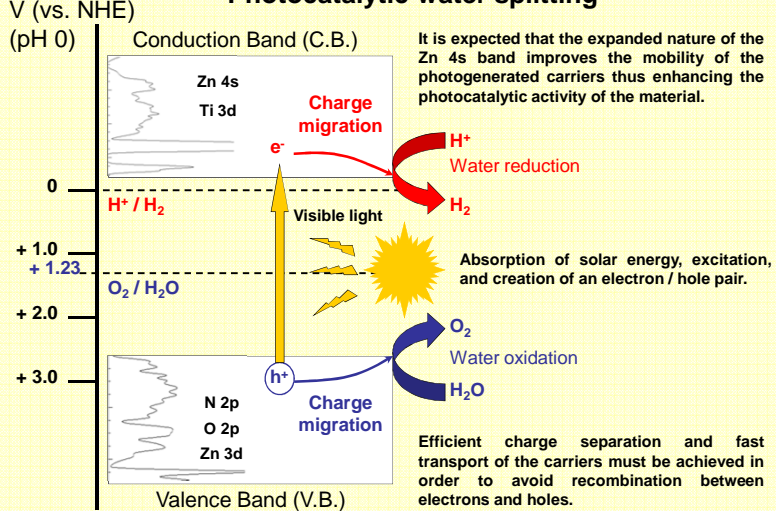
## UV-Vis diffuse reflectance spectra

Diffuse reflectance (%R)



Samples	Temperature	%O	%N	S <sub>g</sub> (m <sup>2</sup> /g)	Optical band gap (eV)	Color
La <sub>2</sub> Zn <sub>1-x</sub> Ti <sub>1+x</sub> (O,N) <sub>6</sub>	Calcination 600°C 2h NH <sub>3</sub> 900°C 10h	17.6	5.0	32 ± 1	2.35	orange
La <sub>2</sub> ZnTiO <sub>6-3x</sub> N <sub>2x</sub>	Calcination 1000°C 2h NH <sub>3</sub> 900°C 10h	18.7	0.5	7 ± 1	3.18	yellow

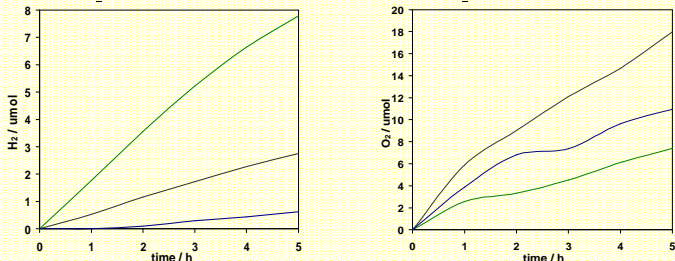
## Photocatalytic water splitting



## Photocatalytic activity

H<sub>2</sub> evolution reaction

O<sub>2</sub> evolution reaction

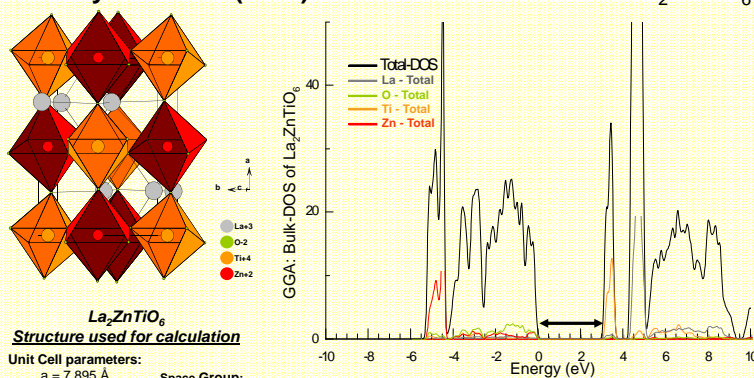


The performance of this new photocatalyst is compared to the reference material LaTiO<sub>2</sub>N.

Time	La <sub>2</sub> Zn <sub>1-x</sub> Ti <sub>1+x</sub> (O,N) <sub>6</sub>		La <sub>2</sub> ZnTiO <sub>6-3x</sub> N <sub>2x</sub>		LaTiO <sub>2</sub> N	
	H <sub>2</sub> (μmol.h <sup>-1</sup> )	O <sub>2</sub> (μmol.h <sup>-1</sup> )	H <sub>2</sub> (μmol.h <sup>-1</sup> )	O <sub>2</sub> (μmol.h <sup>-1</sup> )	H <sub>2</sub> (μmol.h <sup>-1</sup> )	O <sub>2</sub> (μmol.h <sup>-1</sup> )
1 h	1.76	4.03	0	3.88	0.52	5.88
2 h	3.56	6.24	0.10	6.81	1.16	9.03
4 h	6.63	8.40	0.53	9.65	2.27	14.69

\* conditions: catalyst (0.2g); 200ml 20% MeOH; 300 W Xe lamp (>420nm); 0.2 g La<sub>2</sub>O<sub>3</sub>  
 \* conditions: catalyst (0.1g); 200ml 0.02 M AgNO<sub>3</sub>; 300 W Xe lamp (>420nm); 0.2 g La<sub>2</sub>O<sub>3</sub>; 2% Co<sub>2</sub>O<sub>3</sub>

## Density of States (DOS) from GGA calculations for La<sub>2</sub>ZnTiO<sub>6</sub>



Unit Cell parameters:  
 a = 7.895 Å  
 b = 5.5964 Å  
 c = 5.5809 Å  
 β = 90.03°  
 Space Group: P1 21/n 1 (No: 14)  
 Monoclinic  
 DFT: E<sub>gap</sub> = 3.00 eV  
 DR US-VIS: E<sub>gap</sub> ≈ 4.00 eV

Note: complete ordering of Zn/Ti on B-site used for calculation  
 calculation in progress on the oxynitride composition

Iwakura et al., J. Nov. Carb. Res. Sciences, 3 (2011) 1-5

## Conclusion

The development of alternative routes for visible-light-photocatalysis represents a promising challenge where nitride-type compounds can play a major role. Within few years, several advances have been made in the number of phases tested for overall water splitting. With the example of La-Zn-Ti-O-N type phases, we have demonstrated that oxynitrides containing lanthanides, d<sup>0</sup>-type, and d<sup>10</sup>-type metal ions exhibit interesting photocatalytic behavior. The effect of the Zn/Ti ratio on the performance of the oxynitride will be investigated.

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