Flux growth of transition metal oxynitride crystals for photocatalytic water splitting

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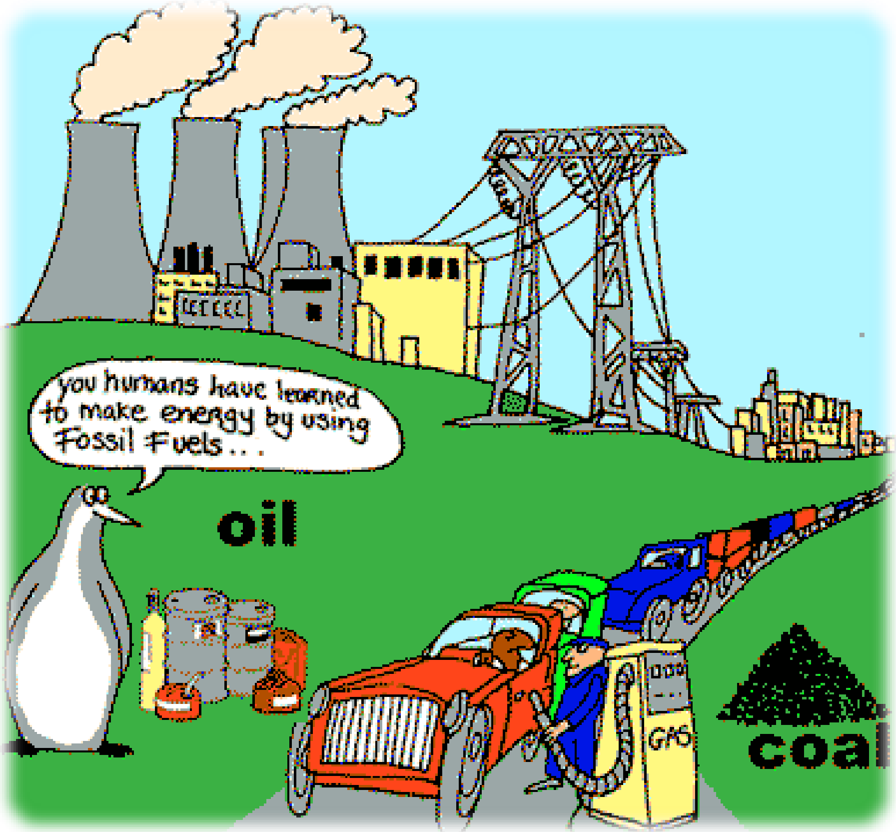
Hydrogen Economy



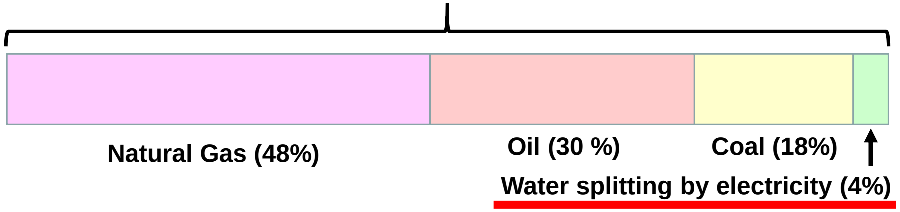
http://tiki.oneworld.net/energy/energy3.html

Hydrogen is a potential zero-emission energy carrier:

Advantages:

- High energy density by weight
- No CO_2 emission
- Large quantity of water on the Earth
- Available solar energy
- Easy mass storage
- Easy long-distance transportation

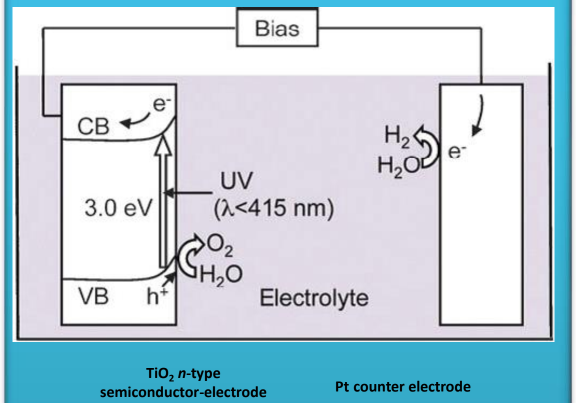
Current global hydrogen production (> 57 mln tons / per year):



The worldwide energy consumption – 57% by 2030

Europe currently leads the world by taking action to moving to a low-carbon economy by 2050.

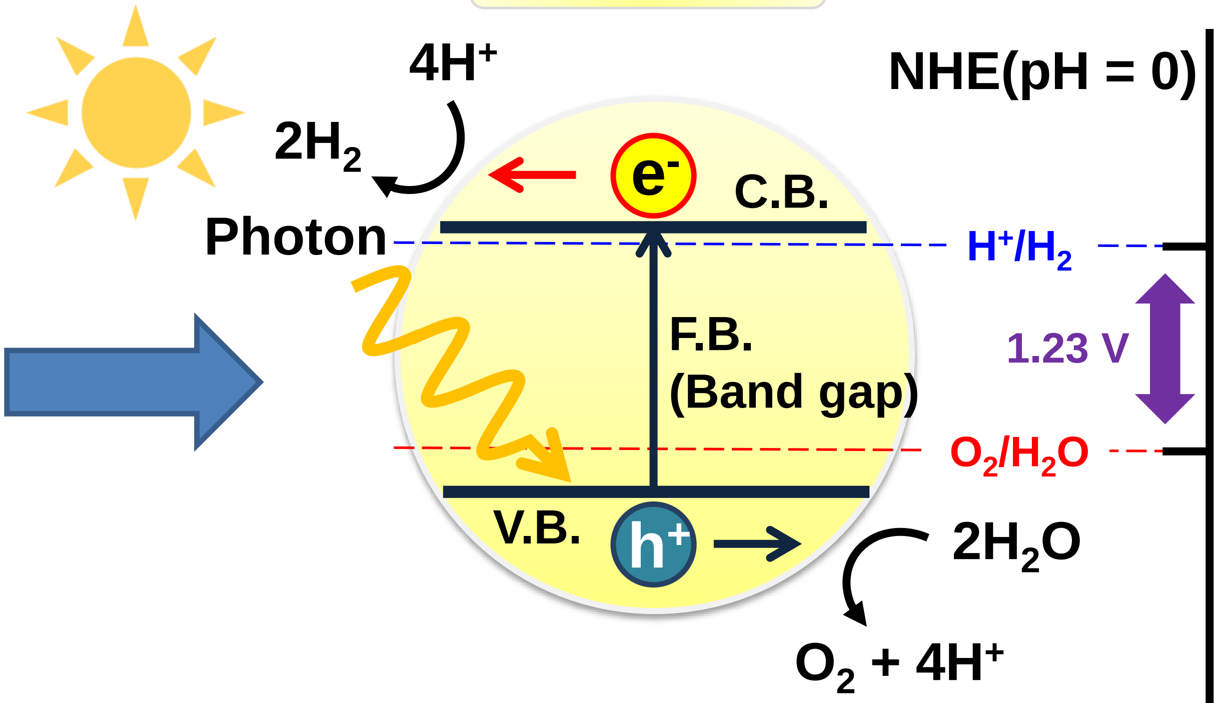
H_2 production using photocatalytic water splitting



Chem. Soc. Rev., **2009**, *38*, 253-278.

Semiconductor-based photocatalytic water splitting using solar energy is economical and green processes to produce hydrogen

$$2H_2O \xrightarrow[\text{Photocatalyst}]{\text{Solar Energy}} 2H_2 + O_2$$



T = 298.15 K, p = 100 kPa
$\Delta G°$ = 237 kJ·mol^{-1}

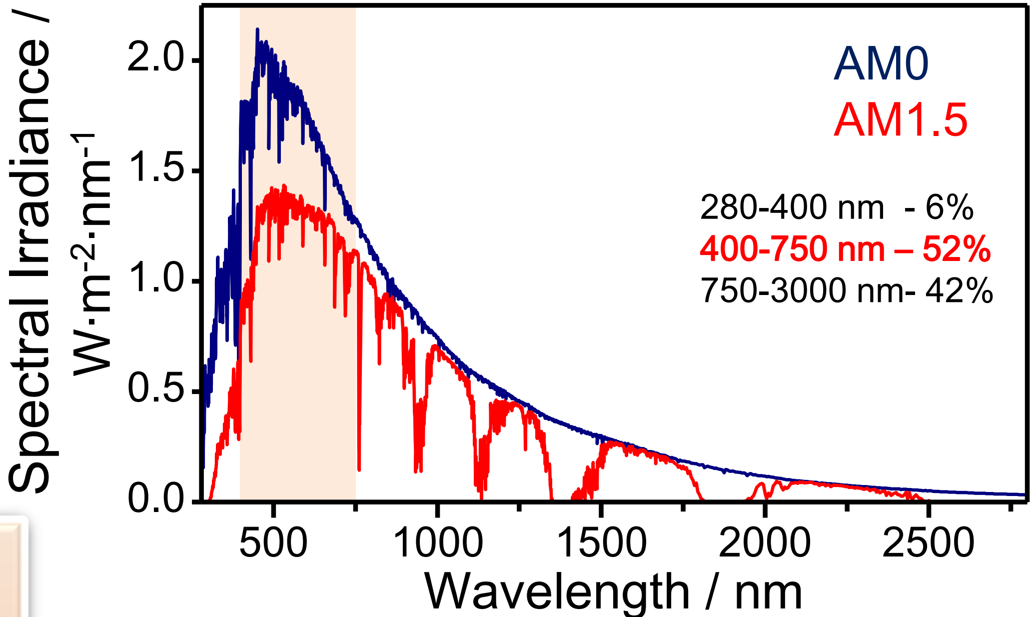
Requirements for photocatalytic materials:

- Chemical stability during the photocatalytic reaction
- Appropriate band structure and band gap
- High crystallinity

Search for visible-light-responsive photocatalysts

UV light active photocatalysts:

TiO_2,
La-doped $NaTaO_3$,
$SrTiO_3$,
$Sr_2Ta_2O_7$,
$Sr_2Nb_2O_7$, $K_2La_2Ti_3O_{10}$, etc.



Visible light active photocatalysts:

Oxide photocatalysts:
WO_3, Fe_2O_3, and $BiVO_4$

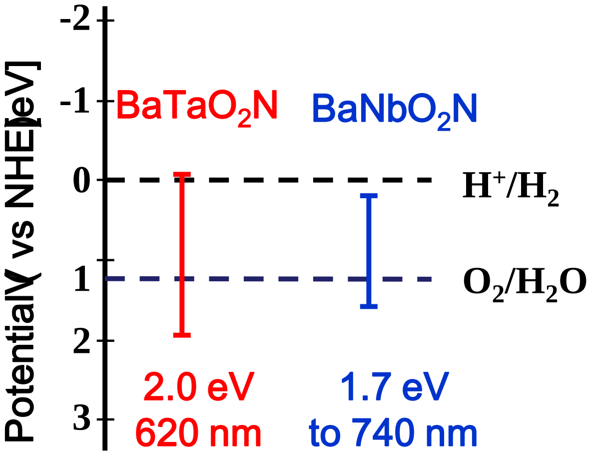
Unsuitable conduction band-edge positions and limited absorption edge wavelength

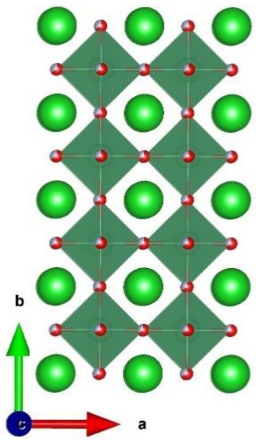
Non-oxide photocatalysts:
Phosphide (GaP)
Sulfide (CdS)
Selenide (CdSe)

For achieving the efficient solar energy conversion, the use of materials having narrow band-gap (E_g < 3.0 eV) is necessary.

less stable during the photocatalytic reaction

Perovskite Oxynitride: $BaNbO_2N$





Energy-level diagrams of $BaTaO_2N$ and $BaNbO_2N$

Balaz et al., *Chem. Mater.* **2013**, *25*, 3337−3343.
Hisatomi et al., *Energy Environ. Sci.* **2013**, *6*, 3595–3599.

Advantages of $BaNbO_2N$:

- contains Nb^{5+} with d^0 electron configuration.
- is composed of abundant metal elements.
- smaller band gap energy (1.7 eV).
- visible light absorbance up to 740 nm.

Main factors for the **low quantum efficiency** of $BaNbO_2N$:

- Poor band alignment of the valence and conduction band edges with respect to the water redox and oxidation potentials.
- Presence of recombination centers that prevent photogenerated carriers from driving the photocatalytic process.

Objective:

The objective of this study was to investigate the effect of the Ta substitution and flux growth method on photocatalytic water splitting activity of $BaNbO_2N$.

FLUX METHOD (MOLTEN SALT)

<u>Flux Method</u> is one of the crystal growth techniques

<u>Advantages:</u>

- Growth of crystals with high quality
- Growth of idiomorphic crystals
- Grow congruently and incongruently melting materials
- Needs relatively simple process
- Environmentally friendly, low-cost
- Has short growth-time scale
- Needs smaller amounts of materials

Rock candy

Solute

Solvent

Dissolution

Time & temperature control

Crystals

Experimental

SOLUTE (50 mol%):
$BaCO_3 + Ta_2O_5 + Nb_2O_5$

FLUX: KCl

Manual mixing for 30 min

Crystal growth step1

Mixing with KCl flux

Crystal growth step2

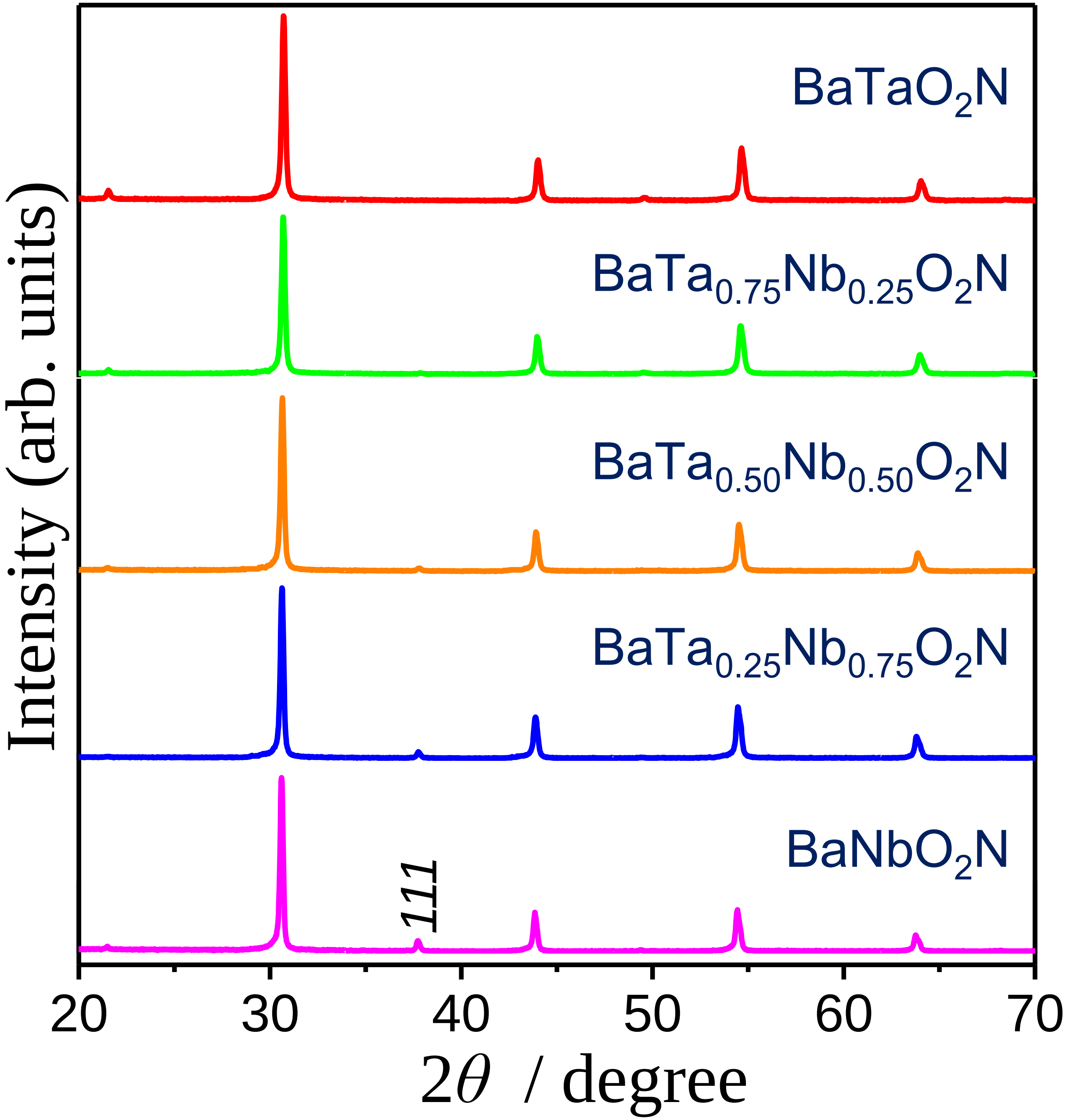
Temperature	900°C
Reaction time	7 h × 2 times
Heating rate	$10^{o}C \cdot min^{-1}$
Cooling rate	natural
NH_3 flow	$200\ ml \cdot min^{-1}$

Acid treatment: (5M HNO_3, 50 mL, 15 min under ultrasonication)

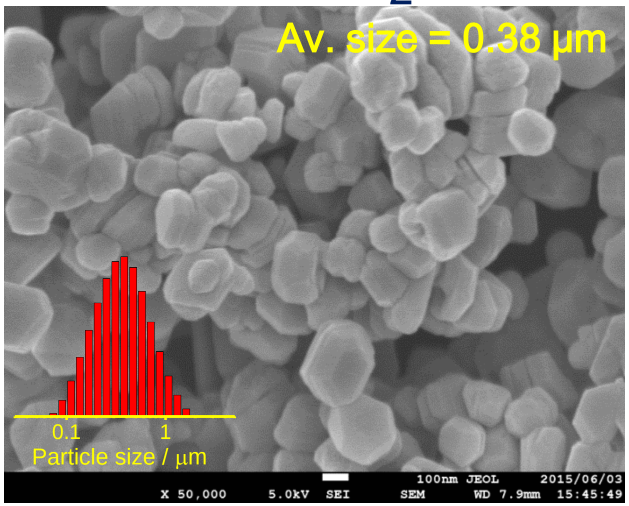
Washing with water using centrifugation

Drying at 100°C for 12 h

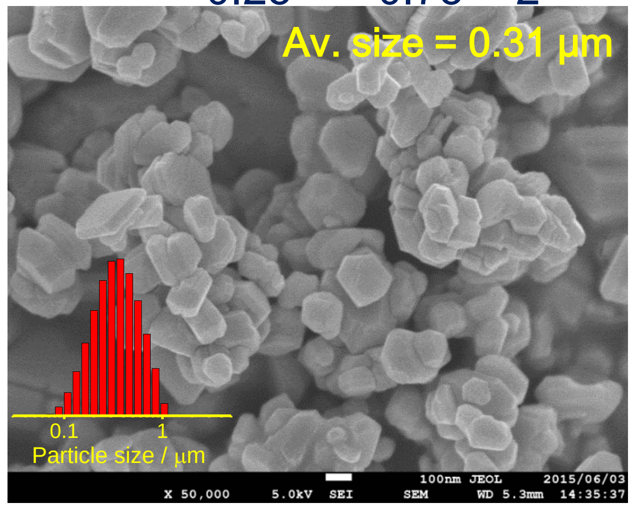
Ta-substituted $BaNbO_2N$ crystals


BaTaO$_2$N
BaTa$_{0.75}$Nb$_{0.25}$O$_2$N
BaTa$_{0.50}$Nb$_{0.50}$O$_2$N
BaTa$_{0.25}$Nb$_{0.75}$O$_2$N
BaNbO$_2$N
111
Intensity (arb. units)
20
30
40
50
60
70
2θ / degree

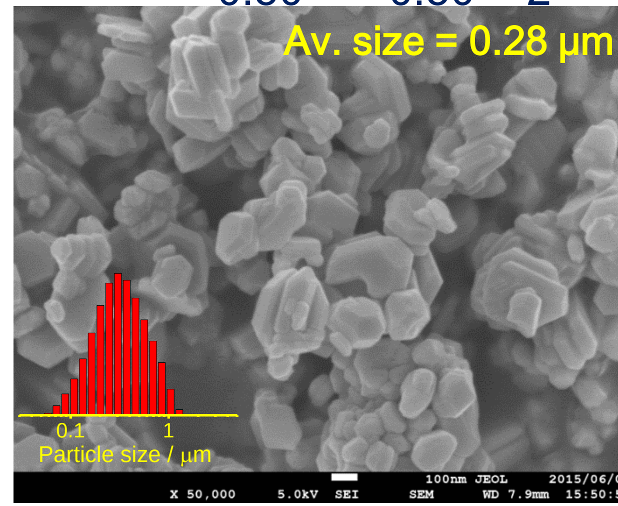
$BaNbO_2N$



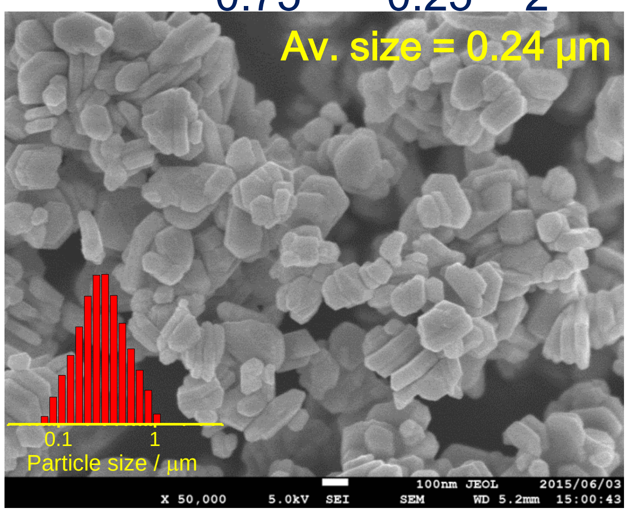
$BaTa_{0.25}Nb_{0.75}O_2N$



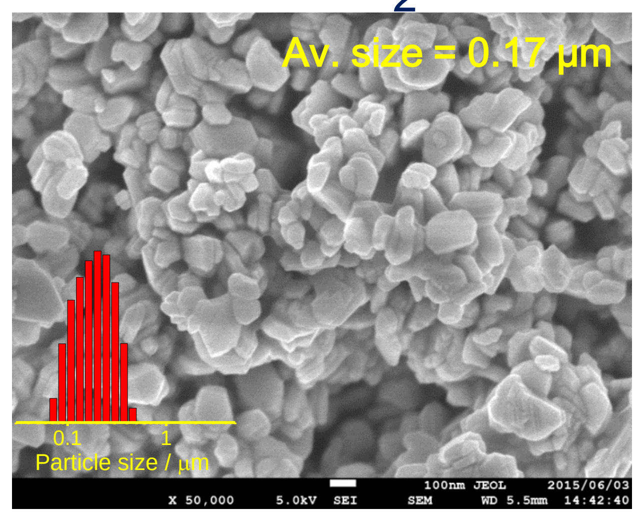
$BaTa_{0.50}Nb_{0.50}O_2N$

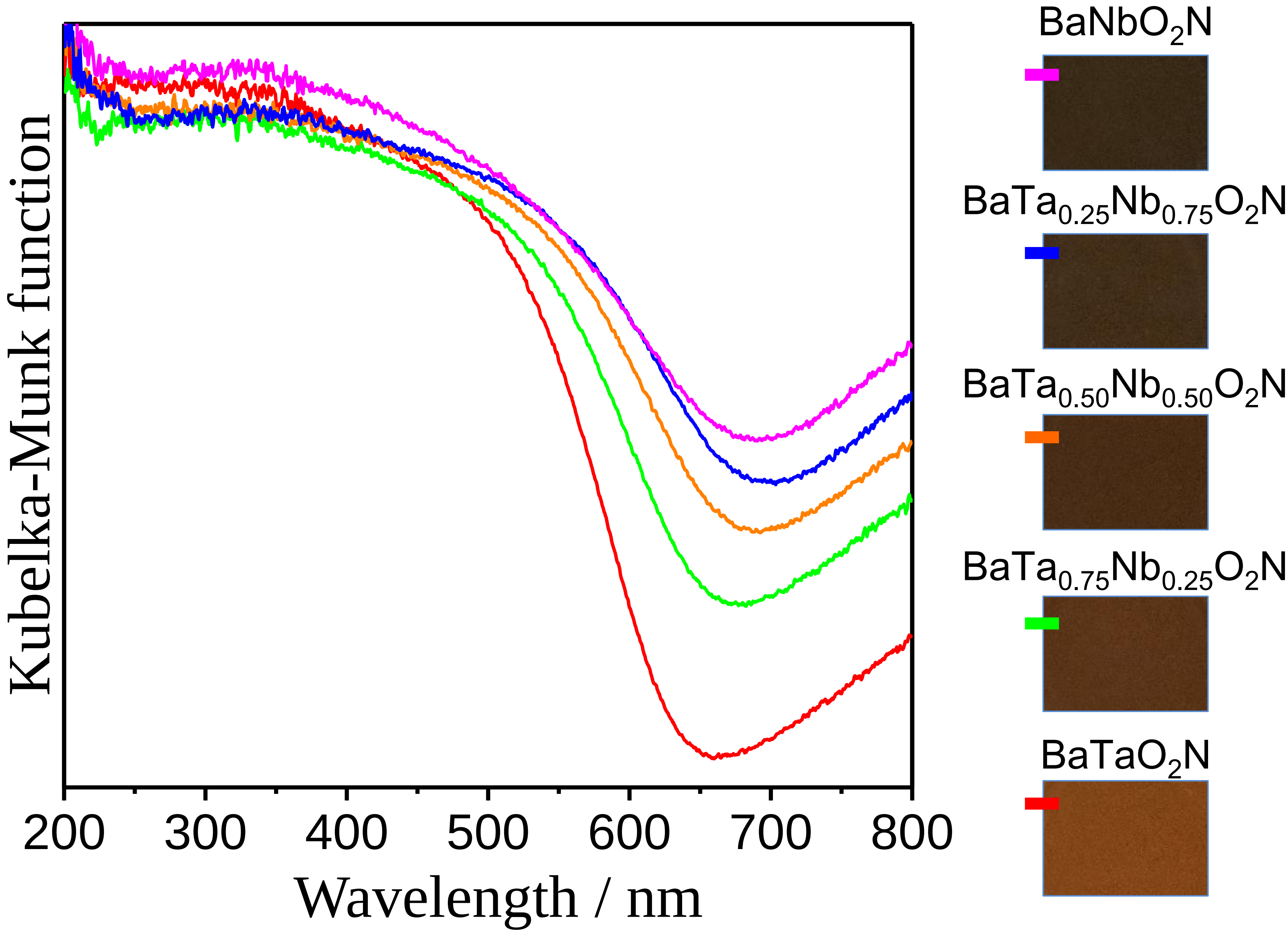


$BaTa_{0.75}Nb_{0.25}O_2N$

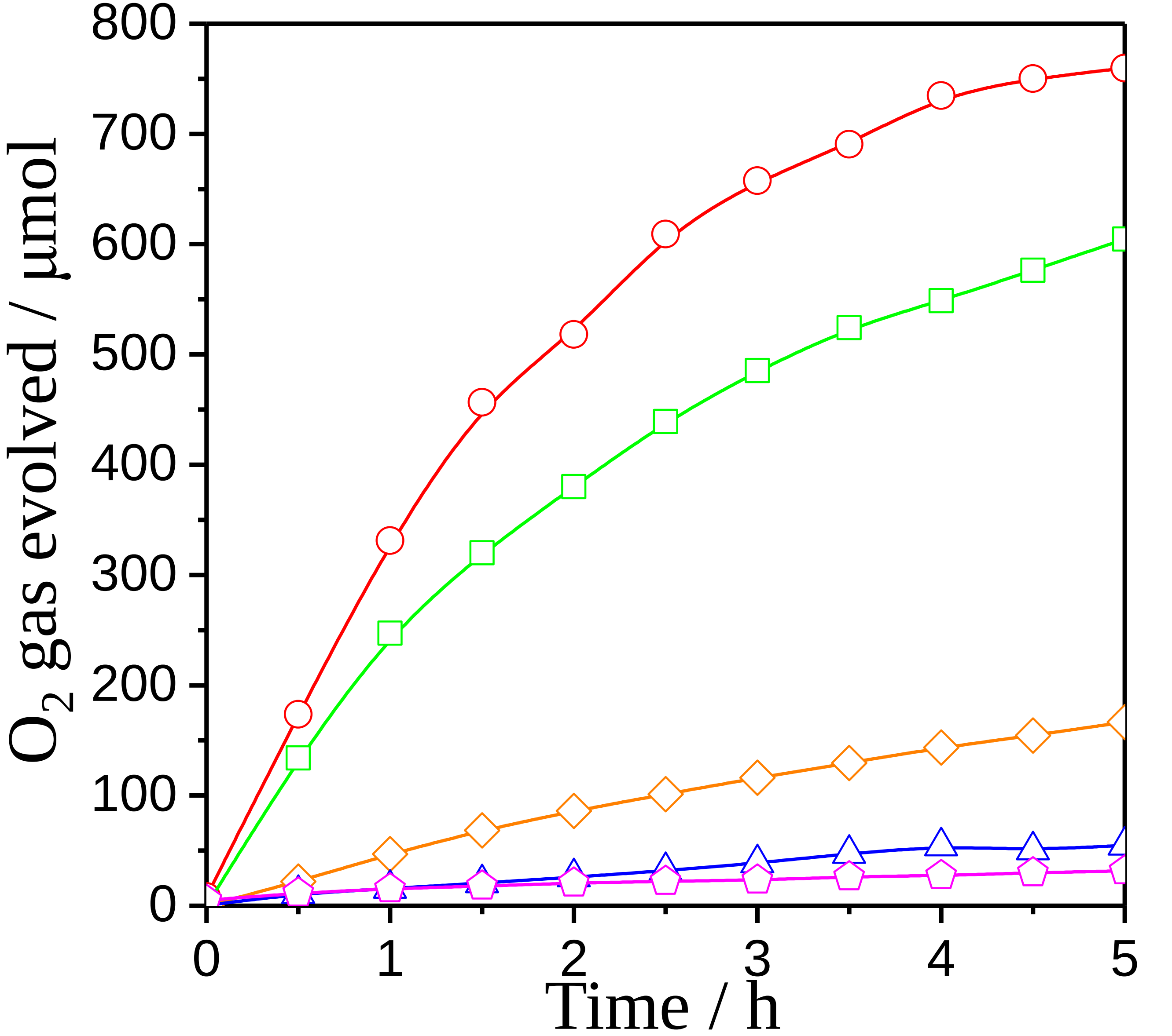


$BaTaO_2N$




Kubelka-Munk function
Wavelength / nm
200
300
400
500
600
700
800
BaNbO2N
BaTa0.25Nb0.75O2N
BaTa0.50Nb0.50O2N
BaTa0.75Nb0.25O2N
BaTaO2N

Water oxidation activity with 2 wt% CoO_x



Rate and S_{BET}

BaTaO$_2$N
6.25 m^2·g^{-1}
152.1 μmol·h^{-1}

BaTa$_{0.75}$Nb$_{0.25}$O$_2$N
6.17 m^2·g^{-1}
121.2 μmol·h^{-1}

BaTa$_{0.50}$Nb$_{0.50}$O$_2$N
5.56 m^2·g^{-1}
33.3 μmol·h^{-1}

BaTa$_{0.25}$Nb$_{0.75}$O$_2$N
6.30 m^2·g^{-1}
10.9 μmol·h^{-1}

BaNbO$_2$N
5.68 m^2·g^{-1}
6.3 μmol·h^{-1}

Acknowledgements

twas

Local organizers and supporters

All my amazing collaborators in the world.

“Science today is global. There is no local science.”

Professor Dan Shechtman
Nobel Prize Winner for Chemistry in 2011

Thank you!

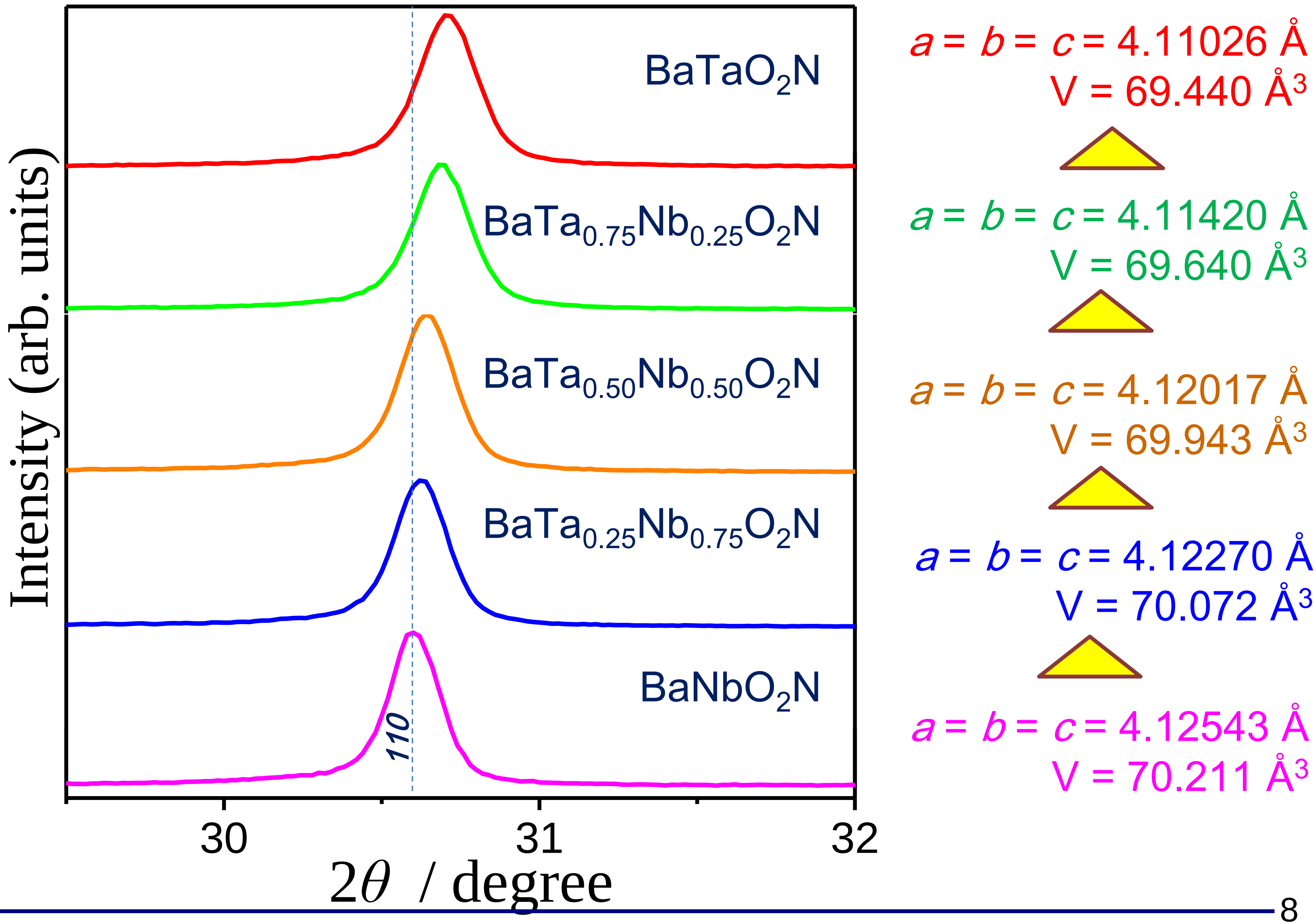
Conclusions

- Tantalum cross-substituted $BaNbO_2N$ crystals were grown directly by an NH_3-assisted flux method.

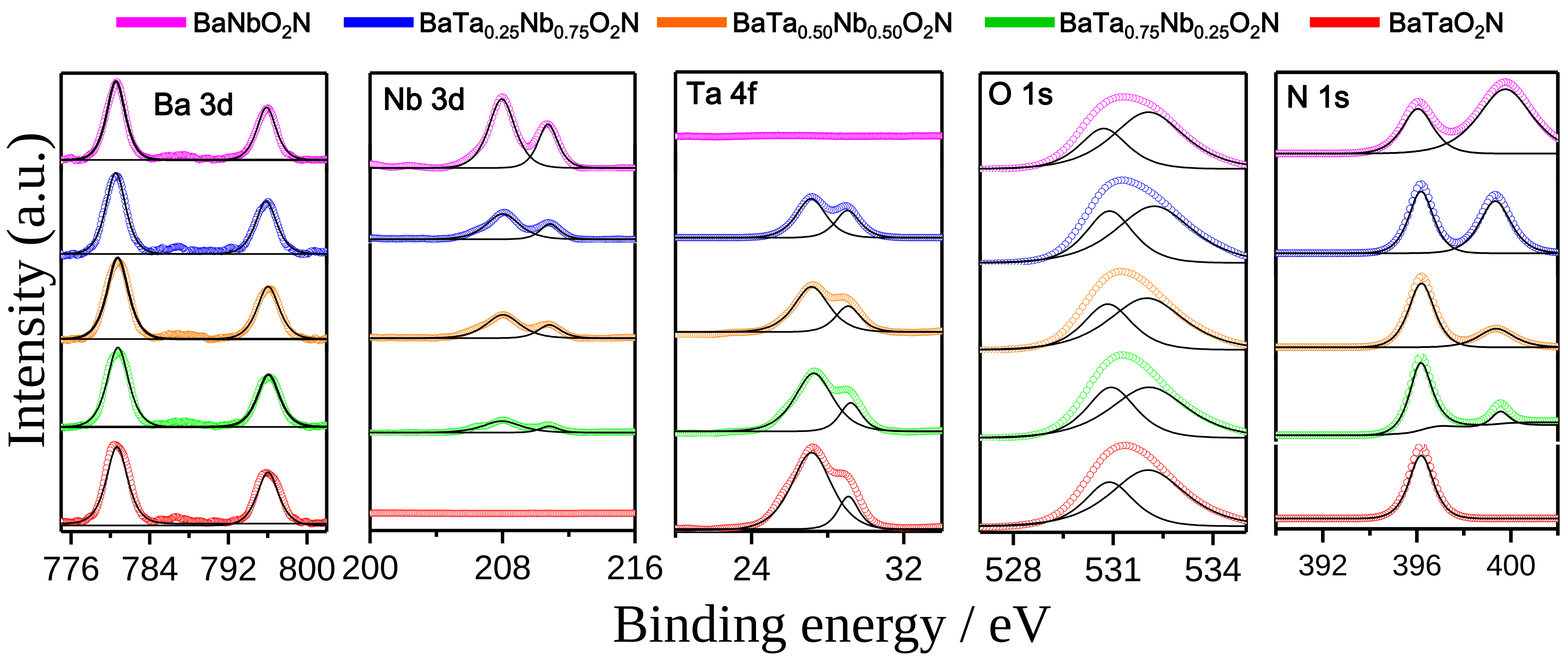
- An increase in the tantalum content resulted in the reduction of the average crystal size from 0.38 to 0.17 μm.

- Intensity of background absorption gradually decreased due to less amount of reduced niobium species and anion deficiency.

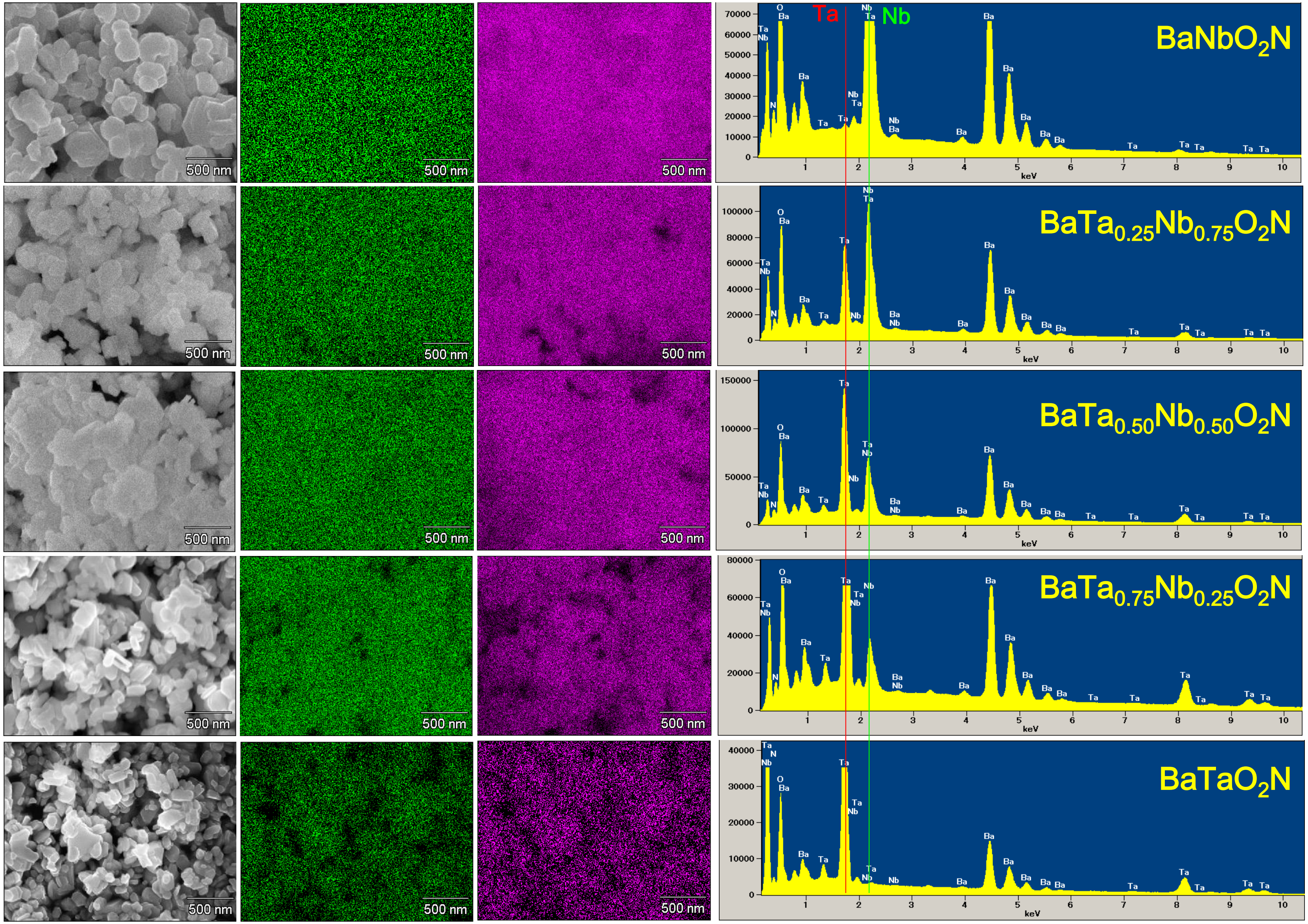
- The oxygen evolution rate of the $BaTaO_2N$ crystals was about twenty five times higher than that of the $BaNbO_2N$ crystals (6.3 μmol·h^{-1}) in this work.


Intensity (arb. units)
BaTaO2N
BaTa0.75Nb0.25O2N
BaTa0.50Nb0.50O2N
BaTa0.25Nb0.75O2N
BaNbO2N
110
30
31
32
2θ / degree
a = b = c = 4.11026 Å
V = 69.440 Å3
a = b = c = 4.11420 Å
V = 69.640 Å3
a = b = c = 4.12017 Å
V = 69.943 Å3
a = b = c = 4.12270 Å
V = 70.072 Å3
a = b = c = 4.12543 Å
V = 70.211 Å3

Sample	Atomic ratio			
	Ba	Ta	Nb	K
$BaNbO_2N$	0.981	0.002	0.998	0.004
$BaT_{0.25}N_{0.75}O_2N$	0.982	0.238	0.762	0.009
$BaT_{0.50}N_{0.50}O_2N$	0.987	0.507	0.493	0.013
$BaT_{0.75}N_{0.25}O_2N$	0.989	0.751	0.249	0.023
$BaTaO_2N$	0.978	0.999	0.001	0.029



BaNbO$_2$N
BaTa$_{0.25}$Nb$_{0.75}$O$_2$N
BaTa$_{0.50}$Nb$_{0.50}$O$_2$N
BaTa$_{0.75}$Nb$_{0.25}$O$_2$N
BaTaO$_2$N
Ba 3d
Nb 3d
Ta 4f
O 1s
N 1s
Intensity (a.u.)
776
784
792
800
200
208
216
24
32
528
531
534
392
396
400
Binding energy / eV



Ta
Nb
BaNbO$_2$N
BaTa$_{0.25}$Nb$_{0.75}$O$_2$N
BaTa$_{0.50}$Nb$_{0.50}$O$_2$N
BaTa$_{0.75}$Nb$_{0.25}$O$_2$N
BaTaO$_2$N
500 nm
keV