Synthesis and characterization of new photocatalytic nano-materials

Presented by

Wanichaya Mekprasart

Nanocomposite Material Research Laboratory (NMRL)

College of Nanotechnology

King Mongkut's Institute of Technology Ladkrabang

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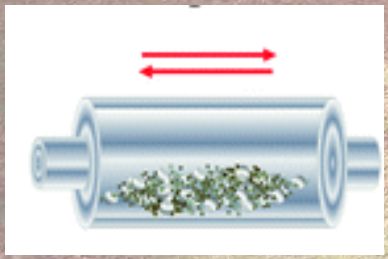

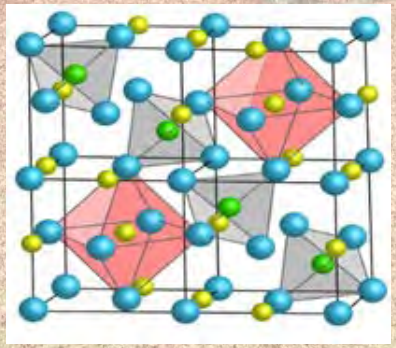

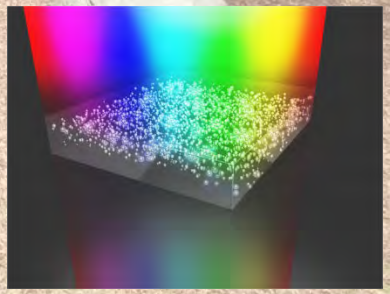

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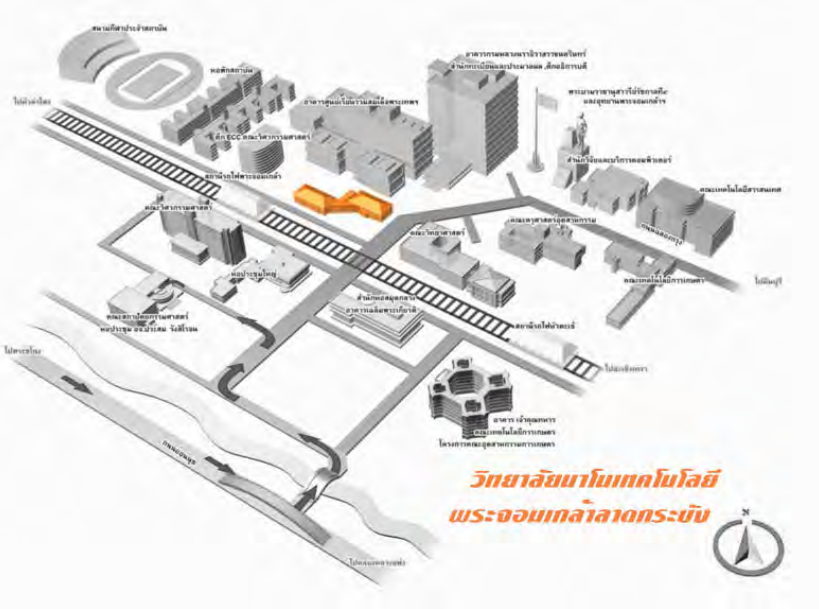

Nanocomposite Material Research Laboratory (NMRL)

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Head of NMRL, KMITL

Dr. Kanokthip Boonyaratkarin

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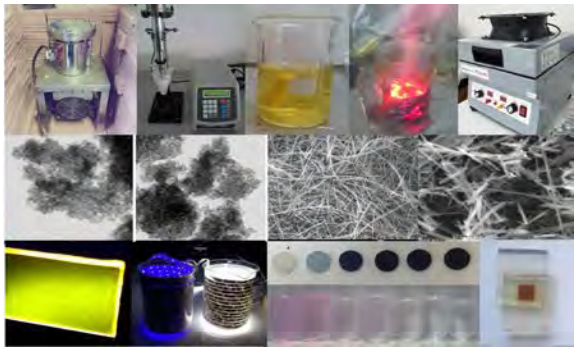


NMRL laboratory is focused on study, research and development of the composite based on oxide materials and nano-scaled materials. Moreover, the products of nanostructured materials synthesized by different processes are the main target that can be proposed to various applications, for example, electronic device, photocatalyst, dye-sensitized solar cell, magnetic-related devices.

Purpose of collaborative research

Prof. Dr. Keiichi N. Ishihara
Social-Environmental Energy Science,
Graduate School of Energy Science

Assoc. Prof. Dr. Wisanu Pecharapa
Nanocomposite Material Research
Laboratory, KMITL

Short research under
JASTIP fund for 2 months
at Kyoto University

Synthesis and characterization of new photocatalytic nano-materials

- Synthesis and development of zinc aluminate ($ZnAl_2O_4$) nanomaterial and its composite utilized as photoluminescence application by rare-earth doping based mechanical milling process
- Synthesis of bismuth oxide optical material via thermal treatment assisted quenching process

Research plan

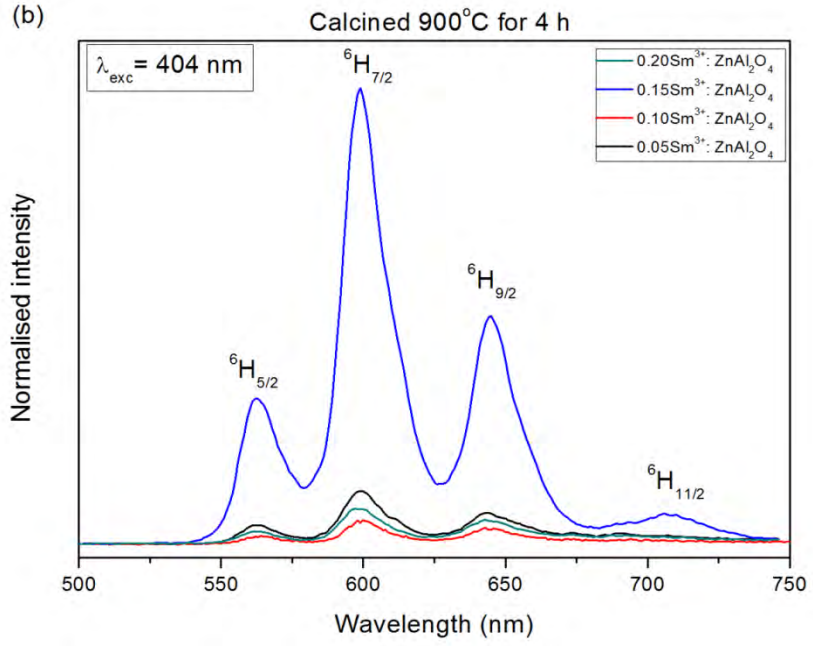
Working sequences	Duration in 2016							
	October				November			
	W1	W2	W3	W4	W1	W2	W3	W4
1. Join in the international conference on Energy and Environment field in ISESES2016	↔							
2. Synthesis of lanthanide element doped zinc aluminate optical material via mechanical vibrational ball milling process assisted with calcination treatment	↔	↔	↔	↔				
3. Characterization of lanthanide element doped zinc aluminate powder via mechanical vibrational ball milling process assisted with calcination treatment		↔	↔	↔	↔			
4. Synthesis of bismuth oxide optical material via thermal treatment assisted quenching process					↔	↔		
5. Learning the experimental setting of photocatalytic degradation system							↔	
6. Comparing of photocatalyst efficiency in methyl orange dye degradation with different phase of bismuth oxide powder							↔	↔

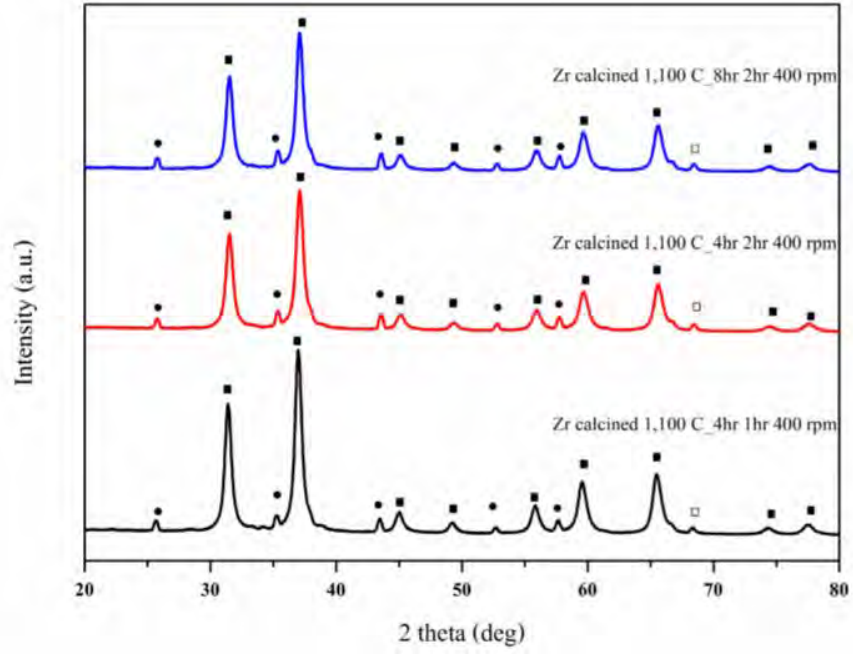
First topic:

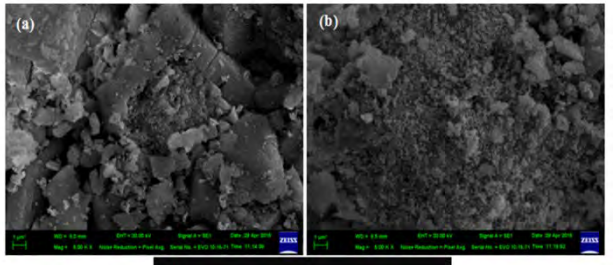
Synthesis and development of zinc aluminate ($ZnAl_2O_4$) nanomaterial and its composite utilized as photoluminescent application by rare-earth doping based mechanical milling process

Research Background in Thailand

- Research in $ZnAl_2O_4$ Synthesis with mechanical system



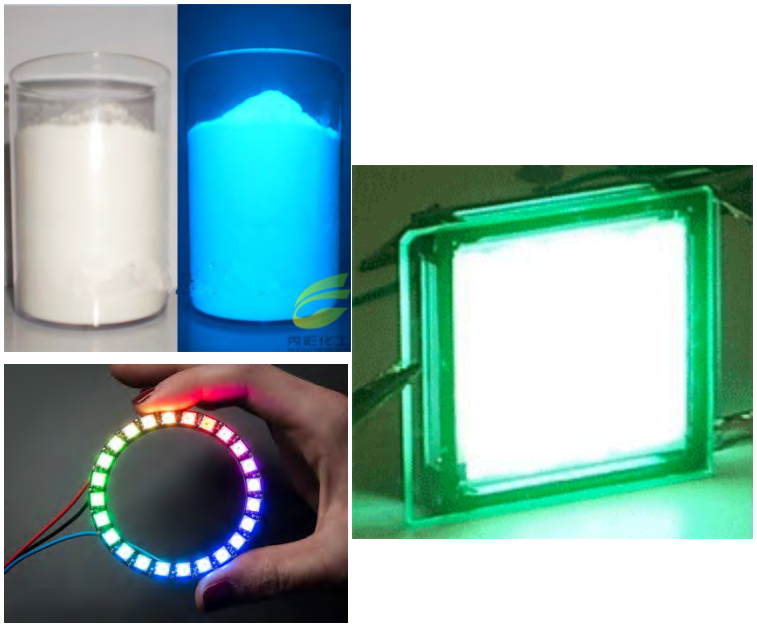


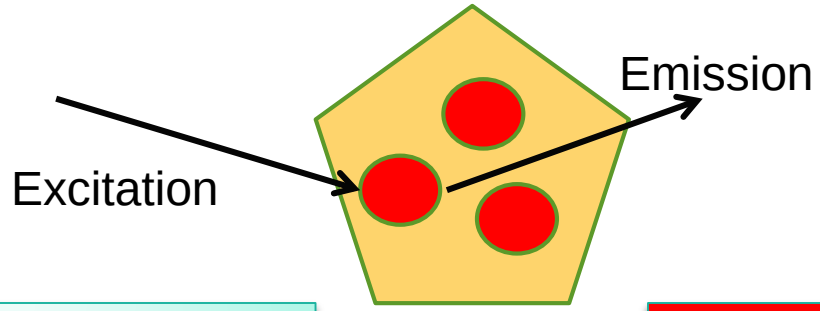


Luminescence Material

Applications

- Field emission display (FED)
- Light-emitting diode (LED)
- Electroluminescent device
- Biological label
- Solid state laser

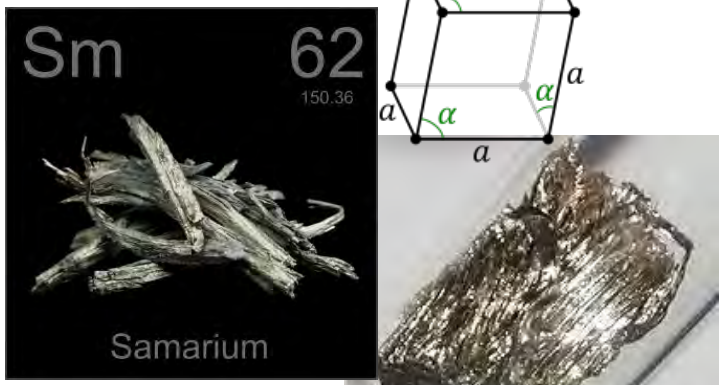


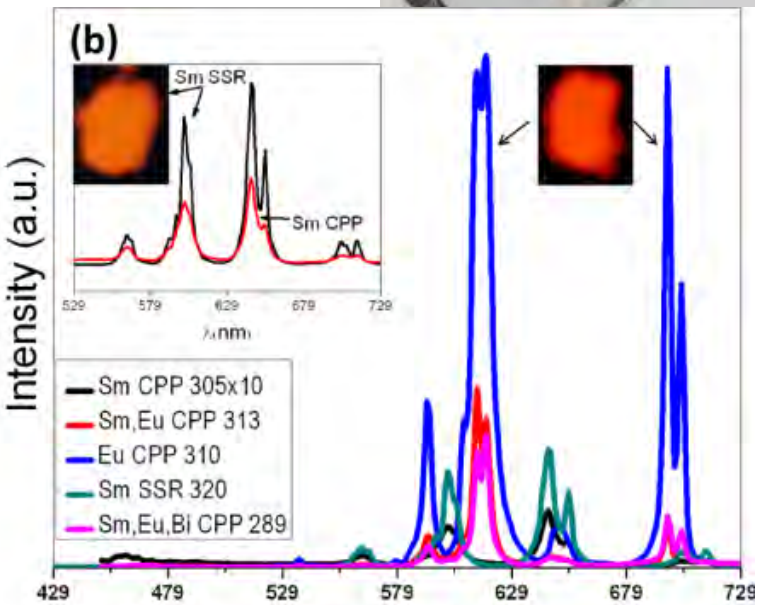


- Rare earth element
- Metal transition element

Luminescence material → **Activator ion** + **Host matrix**

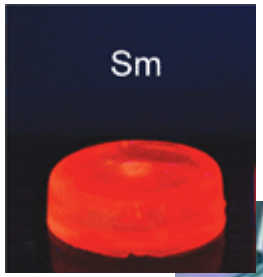
Rare-earth: Samarium (Sm)

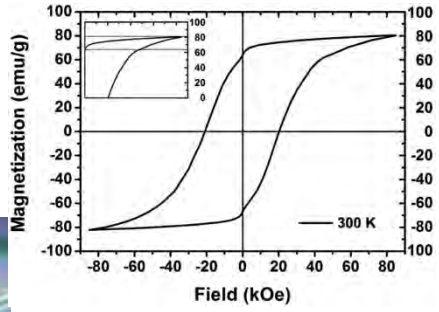




Properties

- Discovered in 1879 by the French chemist Paul Émile Lecoq de Boisbaudran
- A typical member of the lanthanide series
- Oxidation state; +3
- Rhombohedral crystal structure



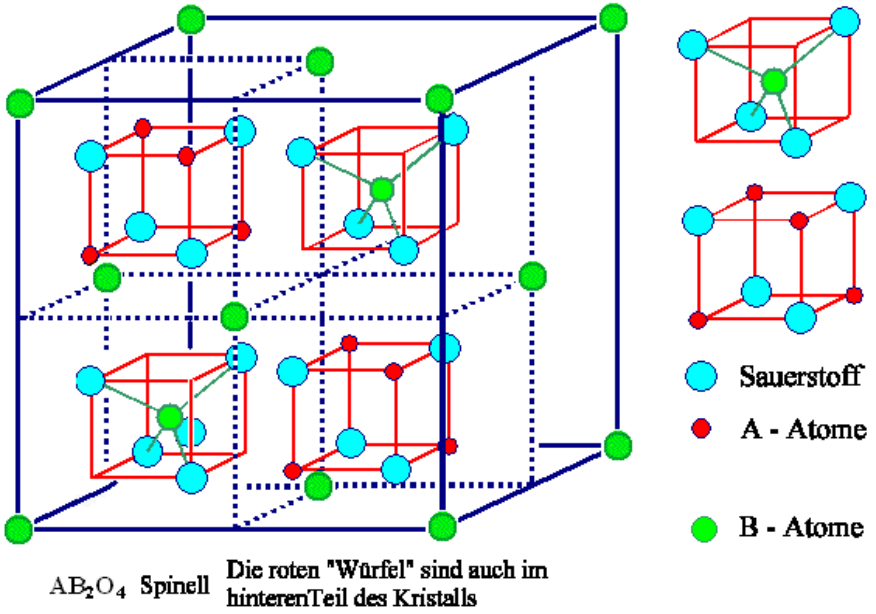


Vineet Kumar et.al, J. Physics D: App. Phys., (2013), 46, 36

Zinc Aluminate ($ZnAl_2O_4$)

Properties

- Name in nature: Gahnite
- Spinel structure (AB_2O_4) and space group Fd3m
- Wide-band gap (3.8 eV)
- Chemical and thermal stability
- High mechanical resistance
- Low surface acidity
- Hydrophobicity



AB_2O_4 Spinell Die roten "Würfel" sind auch im hinterenTeil des Kristalls

Zinc Aluminate ($ZnAl_2O_4$)

Applications

- **High temperature and transparent ceramic material**

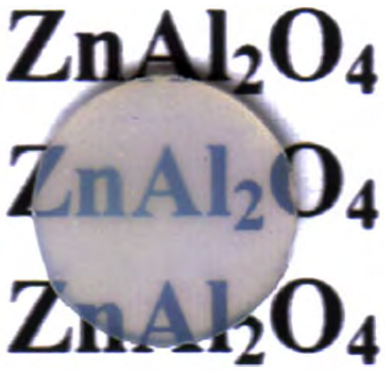
  (X. Yong et.al., Mater. Lett., 123 (2014) pp.142–144.)

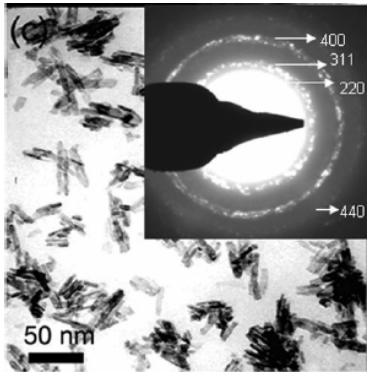
- **Catalyst and catalyst support**

  (M. Zawadzki et.al., Appl. Cata. A 371 (2009) pp. 92–98)

- **Electronic device** (B. Cheng et.al., Ceram. Inter. 39 (2013) pp. 7379–7386)
- **Host matrix for luminescence material**

  (D. Zhang et.al., J. Physic. Chem. Solids 74 (2013) pp. 1131–11305)





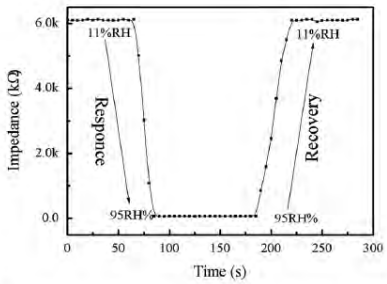
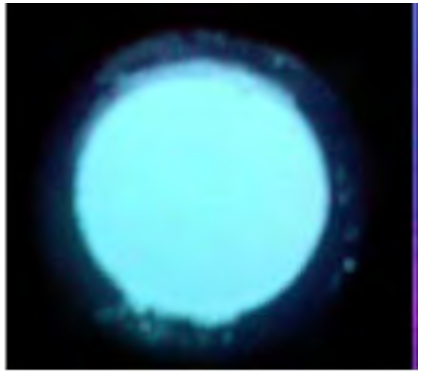
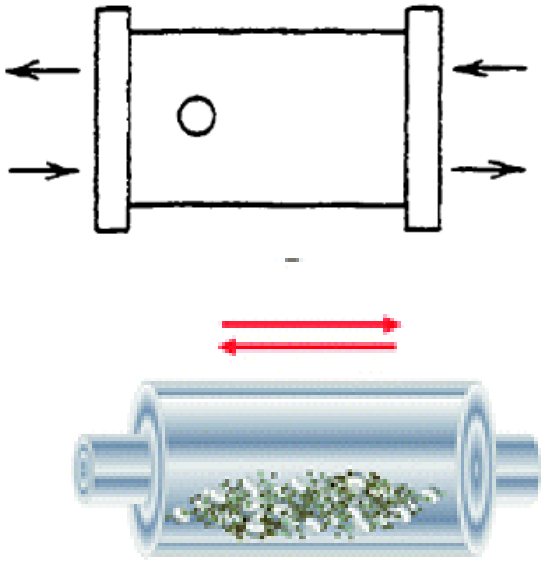


Fig. 6. Response and recovery characteristic of the humidity sensor measured at 100 Hz.



Ball milling process

Vibrational milling



http://pubs.rsc.org/en/content/articlelanding/2013/cs/c3cs35468g/unauth#!divAbstract

Oxide and metal precursor

New phase

(Complex formation)

EXPERIMENTAL

$ZnO:Al_2O_3$ powder at ratio 1:1 (2.5:2.5 g) and Sm metal doping at 0.5, 1 and 2 wt.%

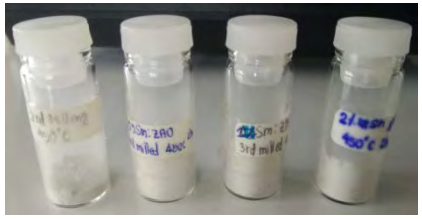
1st Vibrational milling (material: ball weight = 1:10) at 710 rpm for 4 h

3 times

Calciantion; 1200 °C for 6h

3rd Vibrational milling at 710 rpm for 4 h

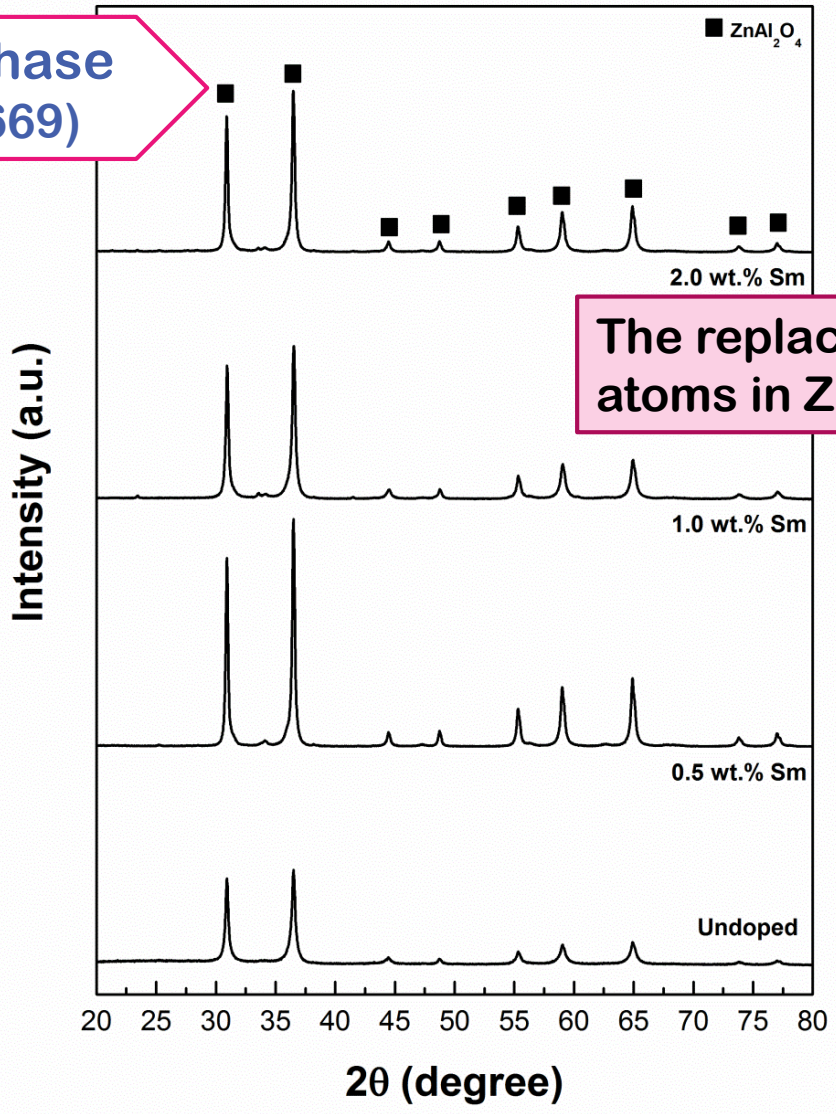
Annealing; 450 °C for 2h



Results: XRD Characterization

$ZnAl_2O_4$ spinel phase
(JCPDF No. 05-0669)

Sm loading

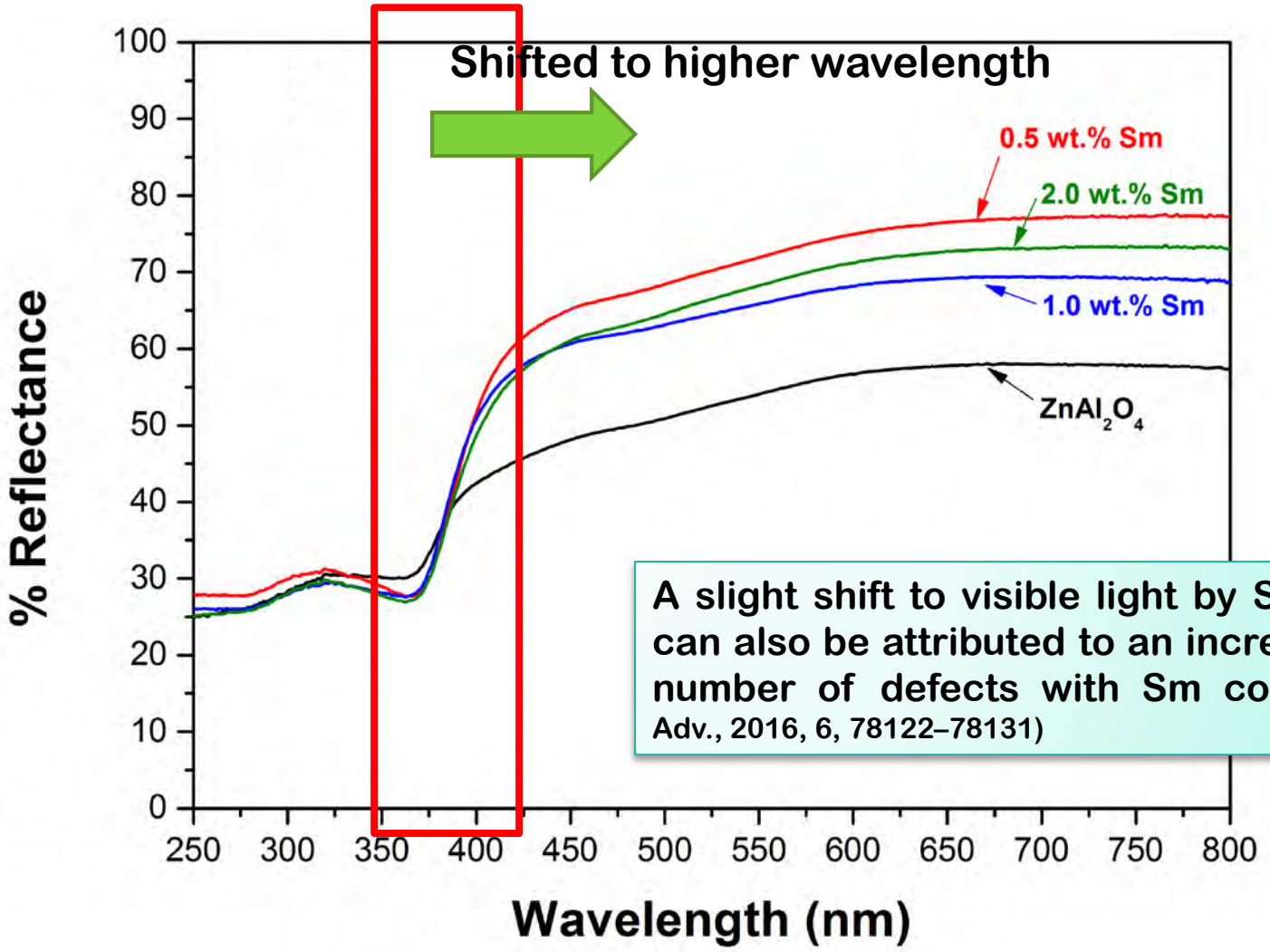


The replacement of partly Sm atoms in Zn atomic position

Crystalline size

Fig. 1. XRD patterns of Sm: $ZnAl_2O_4$ nanopowders with different Sm doping.

Results: UV-Vis Spectra



A slight shift to visible light by Sm:$ZnAl_2O_4$ can also be attributed to an increase of the number of defects with Sm content. (RSC Adv., 2016, 6, 78122–78131)

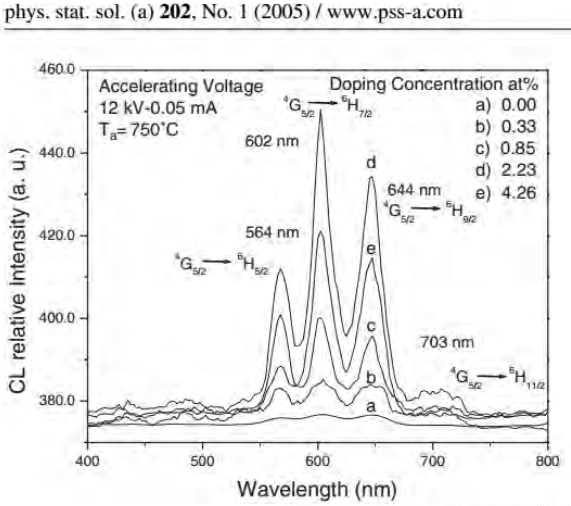
Fig. 3. Diffuse reflectance spectra of Sm:$ZnAl_2O_4$ nanopowders with different Sm doping.

Results: Photoluminescence Spectra

The emission of residual chromium impurity

Sm^{3+} characteristic produced in red-orange region at three strong peaks at 565, 601 and 645 nm

Therefore, Sm defect level acts as the capturing some excited charges relating to energy transfer to luminescence material



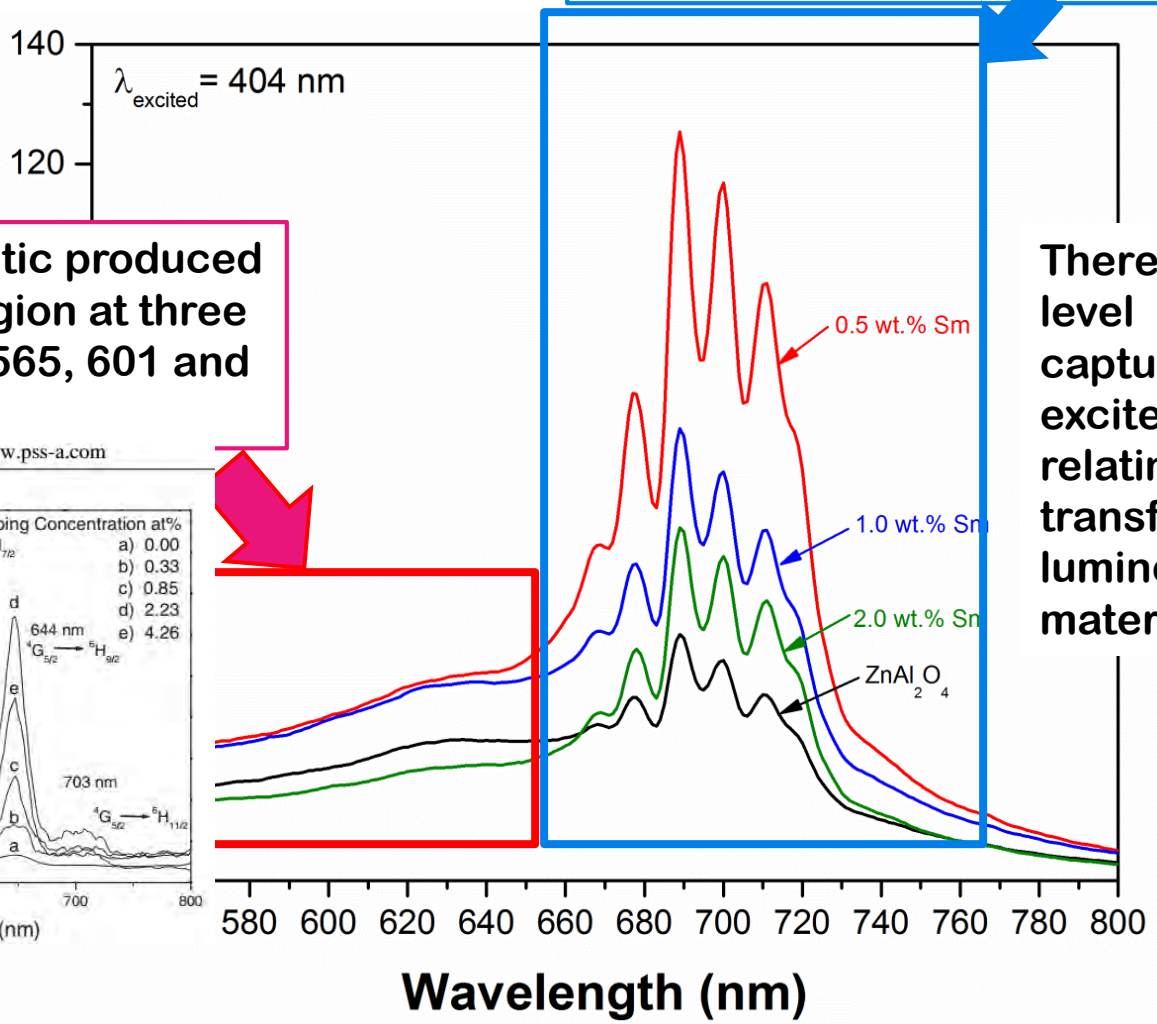


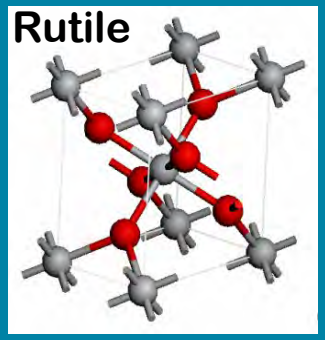
Fig. 4. Photoluminescence spectra of Sm: $ZnAl_2O_4$ nanopowder with different Sm loading.

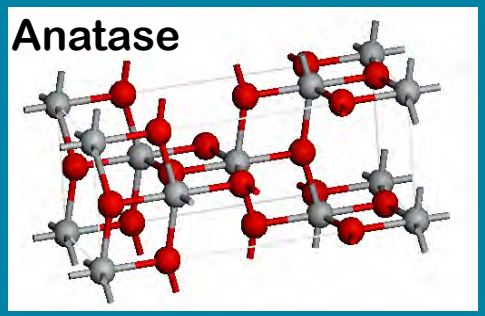
Second topic:

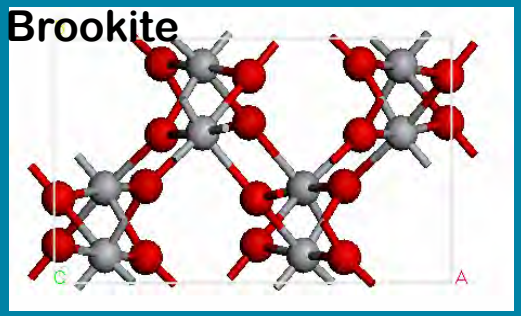
Synthesis of bismuth oxide optical material via thermal treatment assisted quenching process

Titaniumdioxide (TiO_2)

TiO_2 crystalline structures

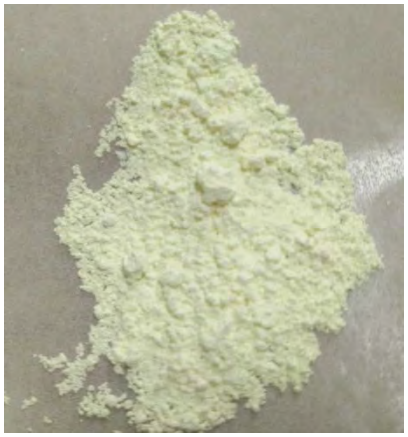




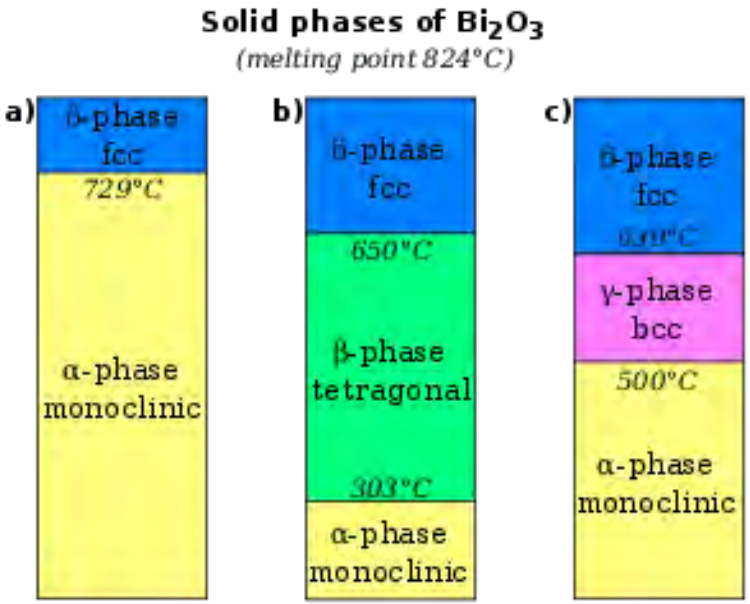


Titaniumdioxide (TiO_2)

Bismuth oxide (Bi_2O_3)

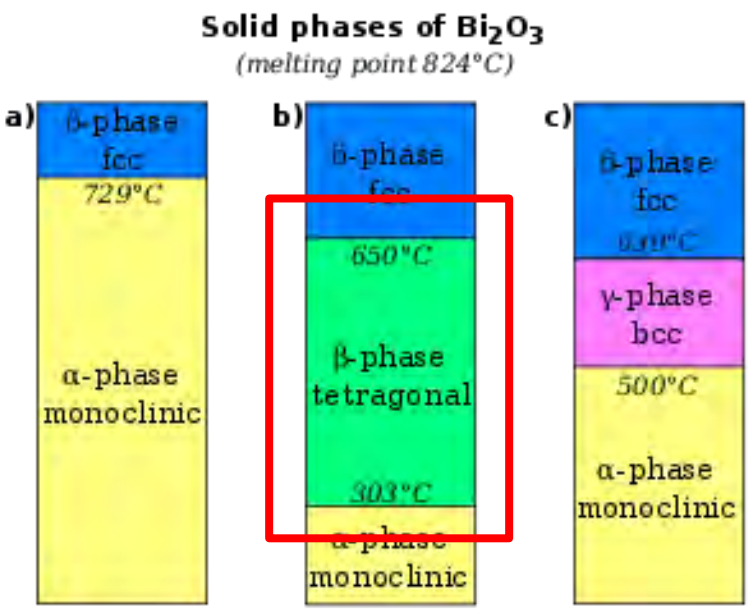


- **Properties**
  - p-type metal oxide semi-conductor
  - Direct band gap of 2.8 eV
  - Visible-light-driven photocatalyst
  - Good electrical conductivity and thermal properties
  - Applied as: gas sensor, phtovoltaic cell, optical coating, fuel cell, etc.



Five polymorphs of bismuth oxide (Bi_2O_3) named: α- Bi_2O_3 (monoclinic),
β- Bi_2O_3 (tetragonal),
γ- Bi_2O_3 (BCC),
δ- Bi_2O_3 (Cubic),
ε- Bi_2O_3 (triclinic).

Bismuth oxide (Bi_2O_3)



- **Photocatalyst**
  - β- Bi_2O_3 show the highest visible-light-driven photocatalyst

Thermal treatment and quenching process

α-, β-Bi_2O_3の固体電子構造解析及び可視光吸収特性評価

古門　裕輝*，中村　裕之，松嶋　茂憲，小畑　賢次

Electronic Structure Analysis and Visible Absorption Characterization of α-, β-Bi_2O_3

Yuki FURUKADO*, Hiroyuki NAKAMURA, Shigenori MATSUSHIMA, and Kenji OBATA

Experimental

$(BiO)_2CO_3$ precursor

Annealed at 370 °C
for 1.5 h

5 °C

Quenching process

20 °C

beta (β)-Bi_2O_3

alpha (α)-Bi_2O_3

Fig. 5 Photographs of Bi_2O_3 powders by via thermal treatment at different temperature (a) $(BiO)_2CO_3$ precursor, (b) 5 °C and (c) 20 °C.

Results: XRD Characterization

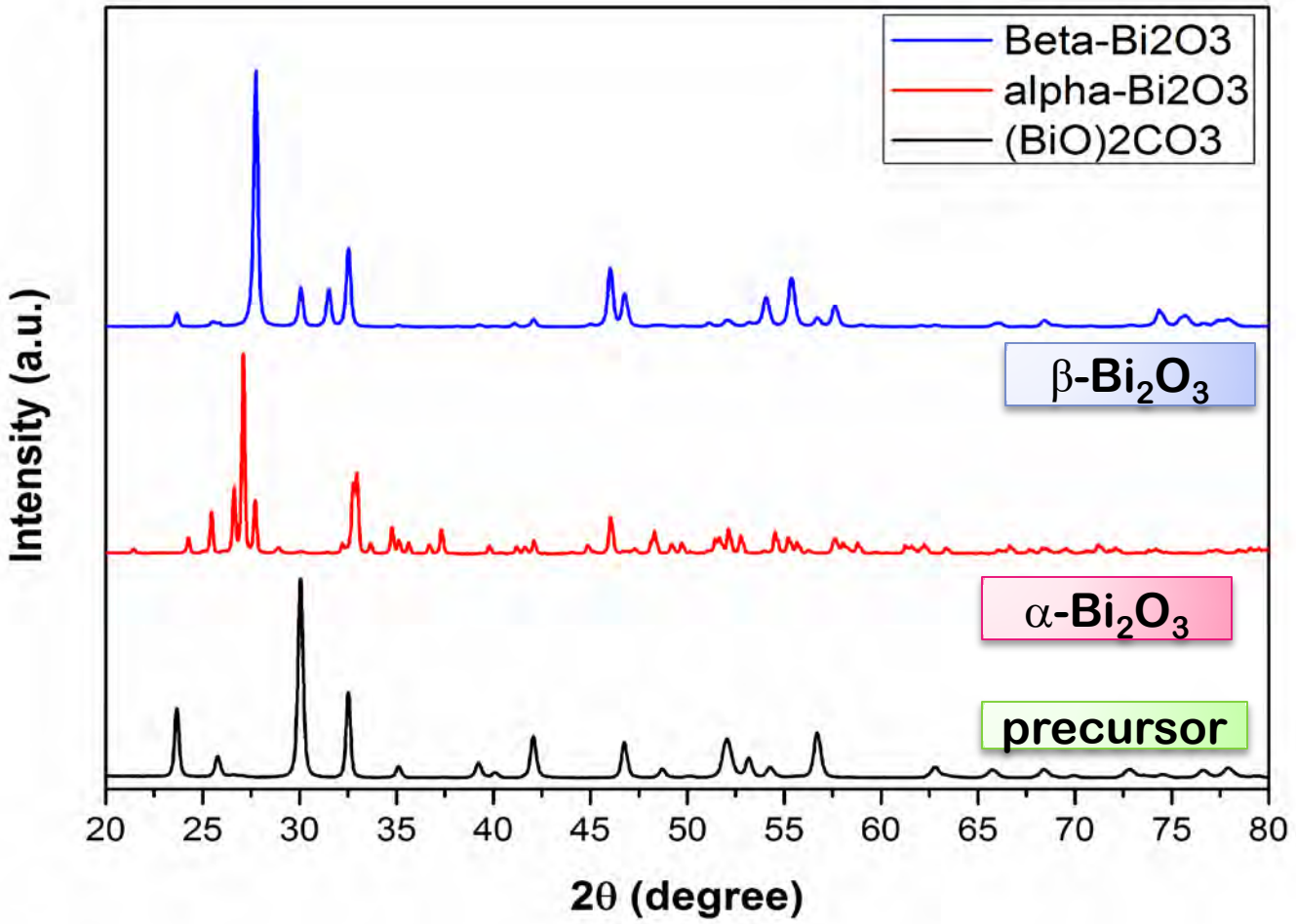


Fig. 6 XRD patterns of (a) $(BiO)_2CO_3$ precursor and the products of (b) alpha-Bi_2O_3 and (c) beta-Bi_2O_3 powder at different quenching temperatures.

Results: UV-Vis Spectra

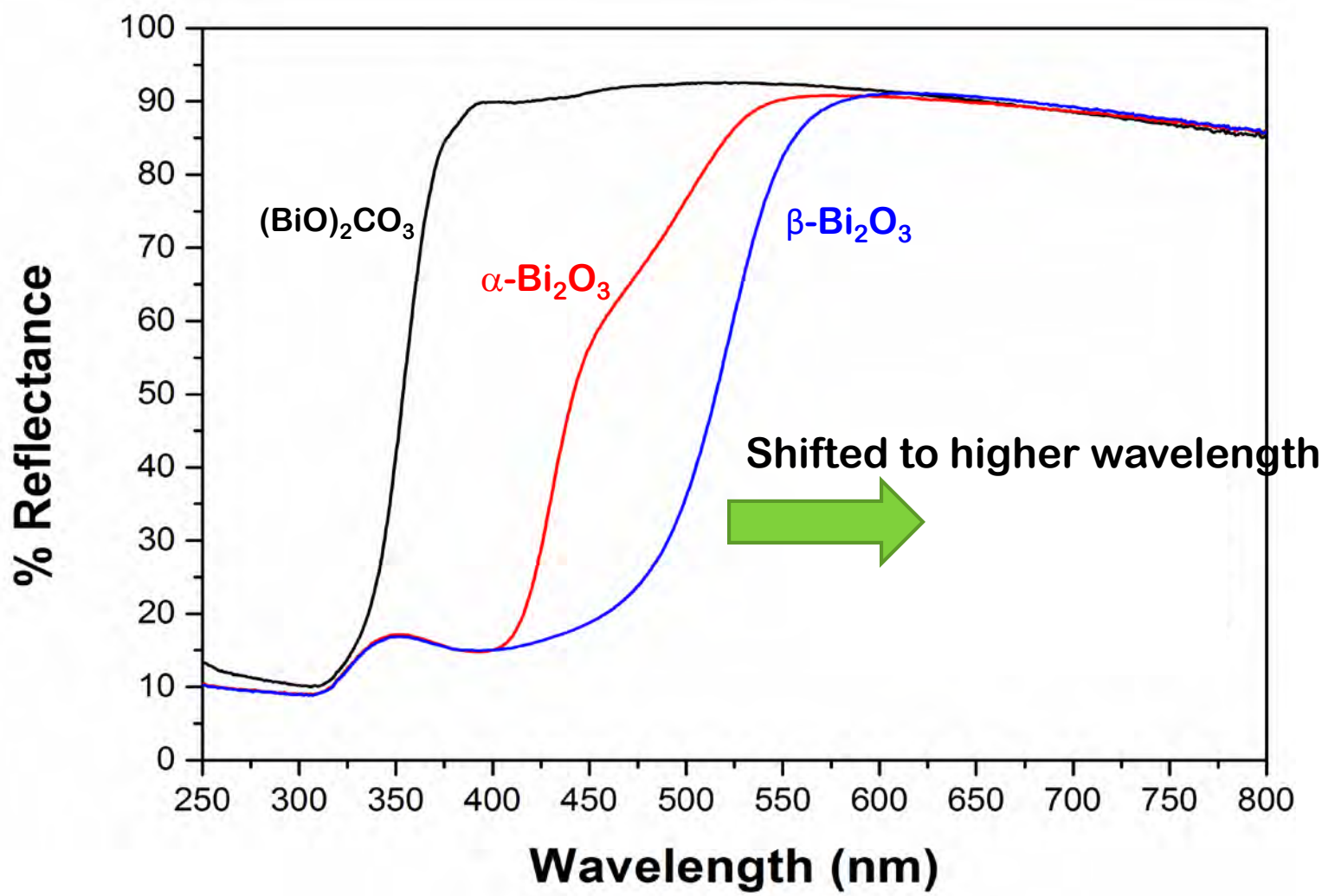
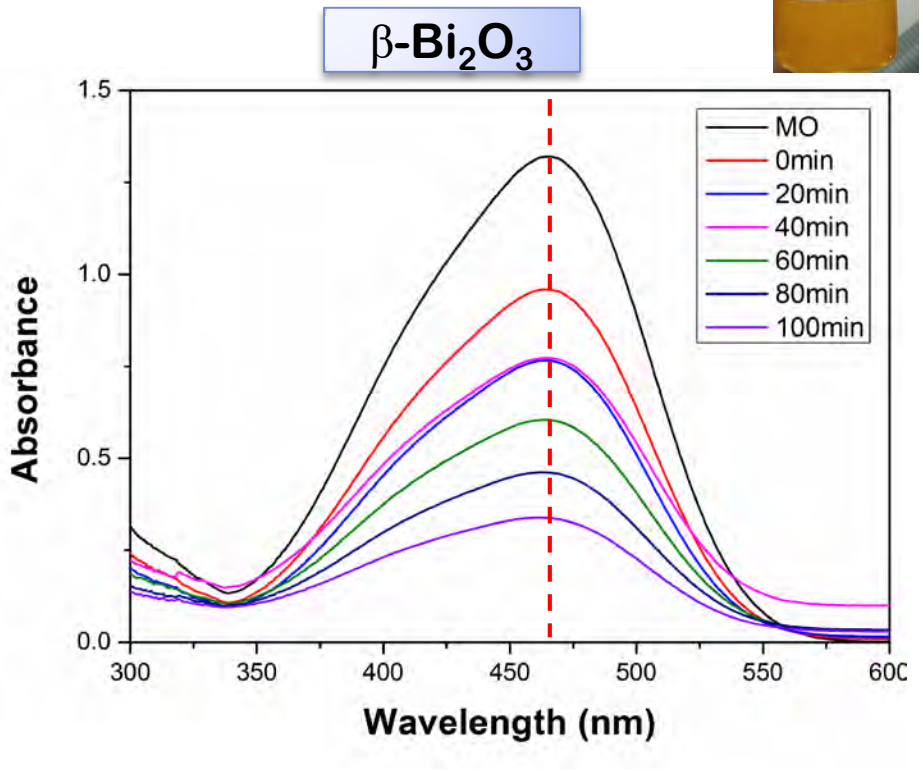


Fig. 7 Diffuse reflectance spectra of (a) $(BiO)_2CO_3$ precursor and the products of (b) alpha-Bi_2O_3 and (c) beta-Bi_2O_3 powder at different quenching temperatures.

Results: Photcatalytic activity



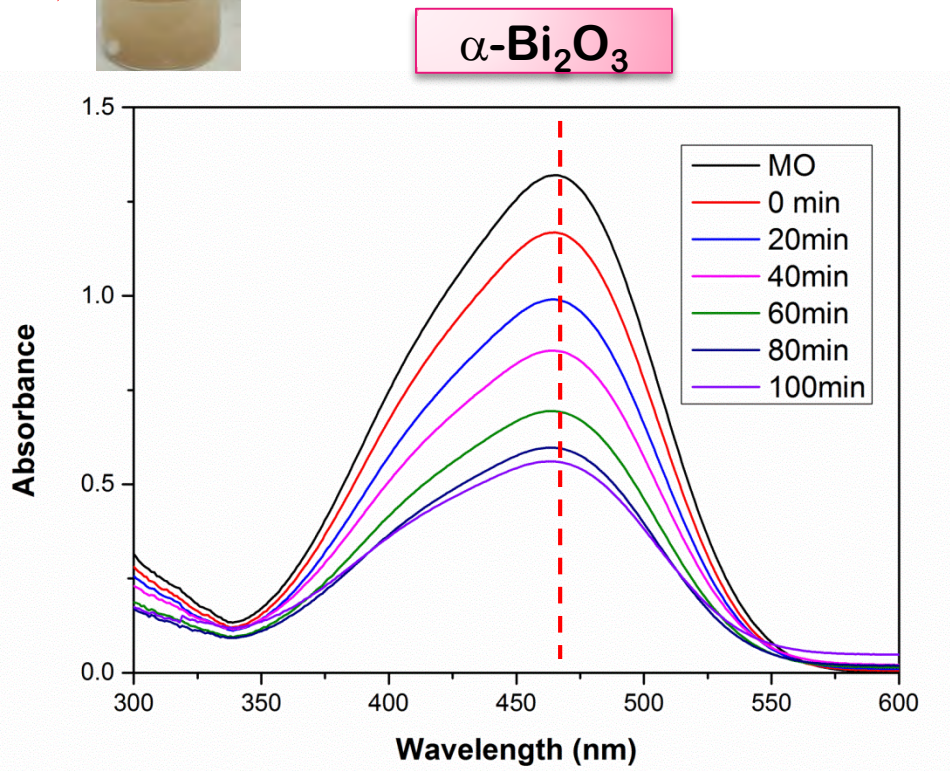


Fig. 8 Absorption spectra of Methyl orange (MO) under Xenon lamp irradiation using β and α - Bi_2O_3 photocatalyst.

Results: Photcatalytic activity

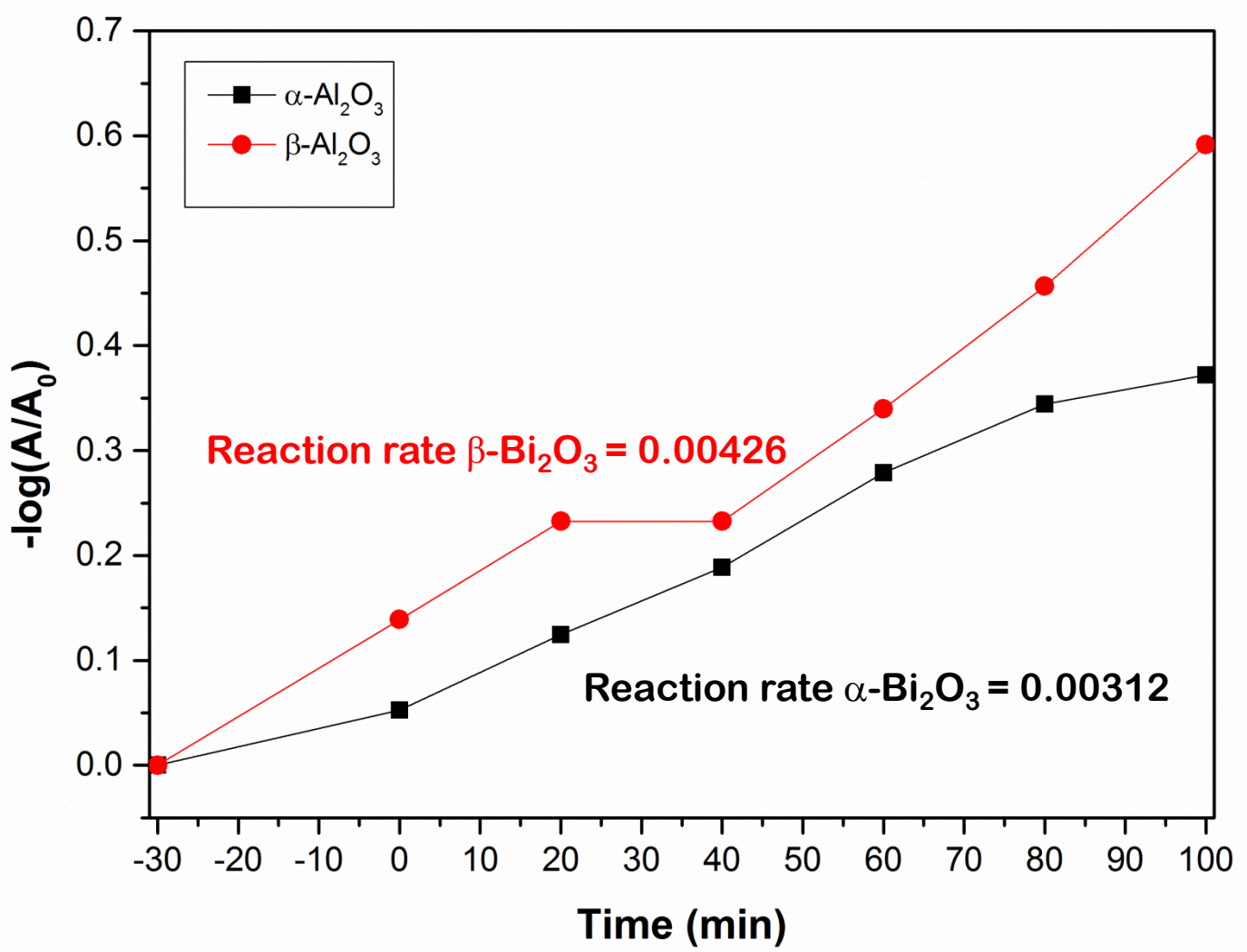


Fig. 9 Reaction rate of α and β Bi_2O_3 photocatalyst in MO degradation.

Conclusion

- The improvement of $ZnAl_2O_4$ new product has been synthesized by solid-state reaction assited with calcination process (several milling and thermal process).
- The strongest emission was performed at 0.5 wt.% Sm in $ZnAl_2O_4$ owning to the energy transfer from Sm to $ZnAl_2O_4$ matrix.
- Bi_2O_3 powders in β and α phase were successfully prepared from $(BiO)_2CO_3$ precursor by facile process of heat treatment assisted with quenching process.
- Owing to high absorption in visible region, β-phase Bi_2O_3 can efficiently active in the catalytic performance in the photodegradation of aqueous MO.