Moscow University Seminar

February 14, 2013

Atomic Structures and Chemistry of Materials Interface

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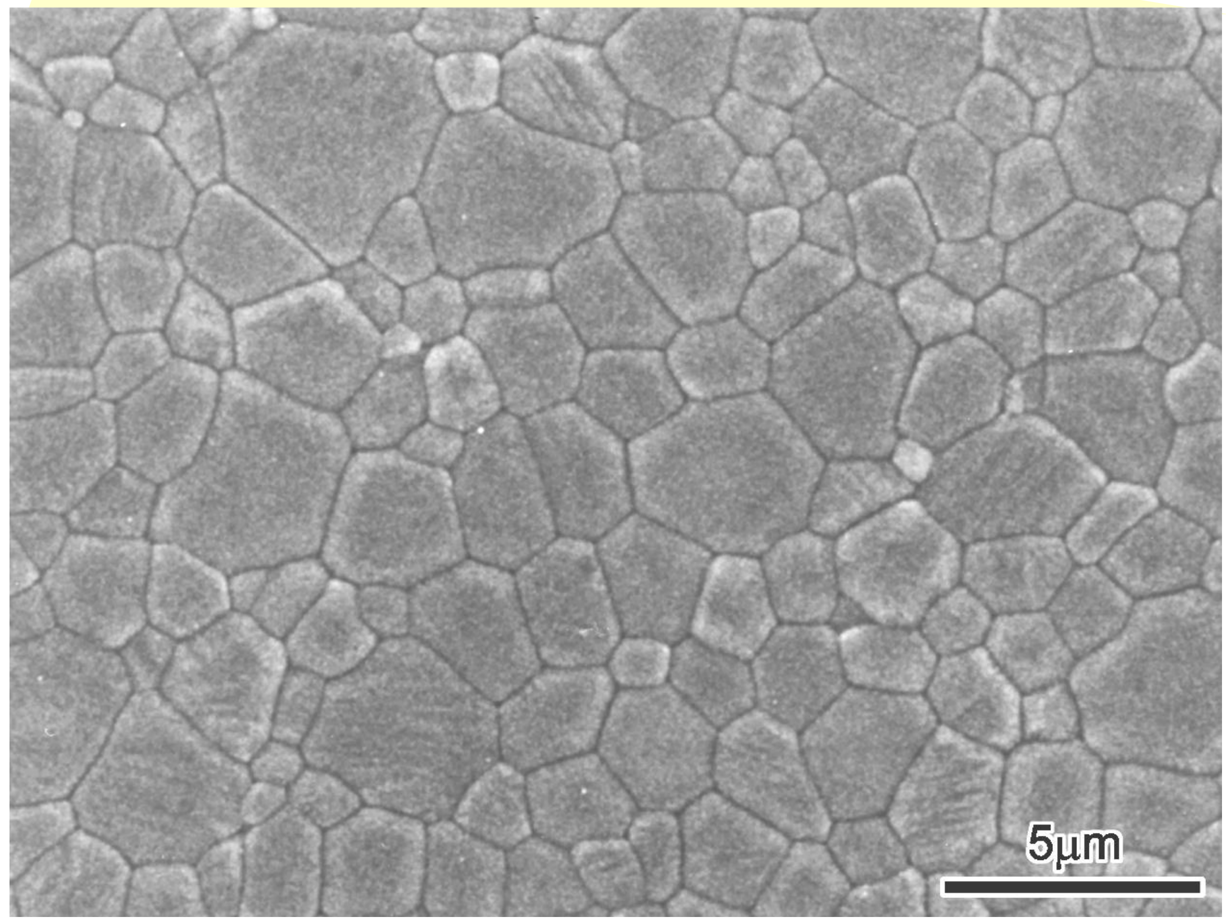
東京大学 THE UNIVERSITY OF TOKYO

NSRL

wpi World Premier International Research Center Initiative

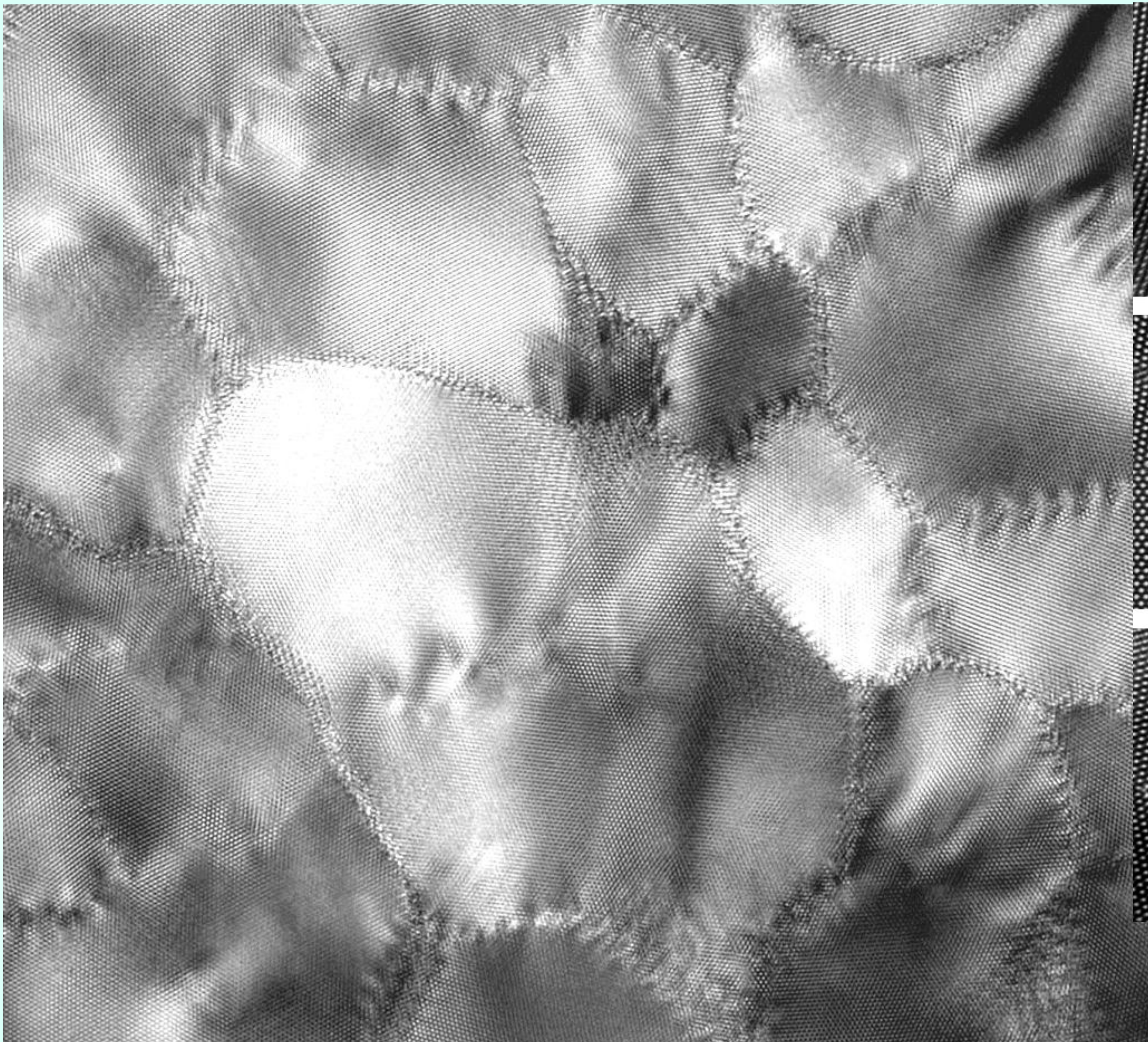
Environment
Energy
Sensor
Liquid Crystal
Chip Coil
Thermistor
Safety
IT
IC Substrate
Varistor
Condenser
Dielectric
Li ion battery

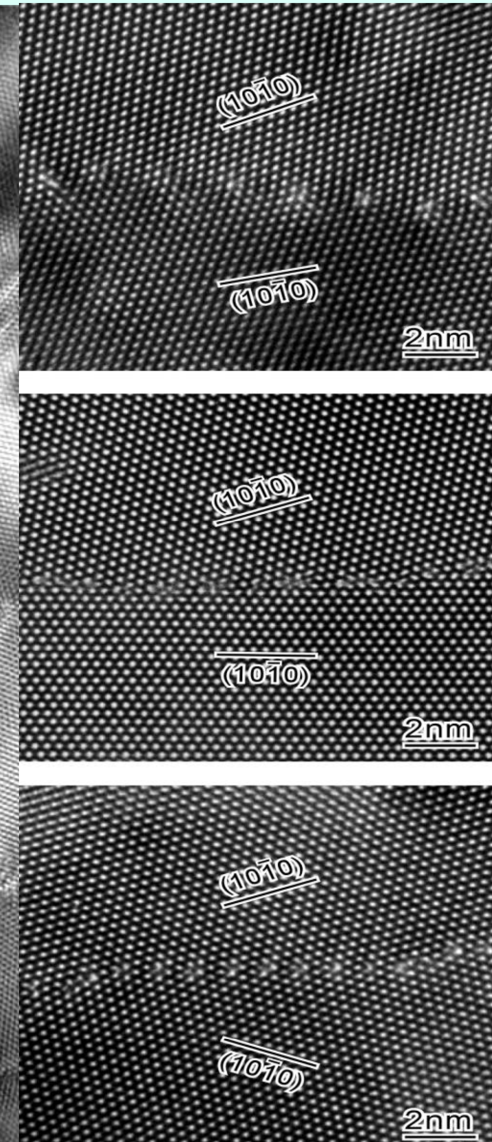
Polycrystals－Grain Boundary



HRTEM (ZnO Film)

Grain Boundary Character





PRB (2004)

Dopant Effect

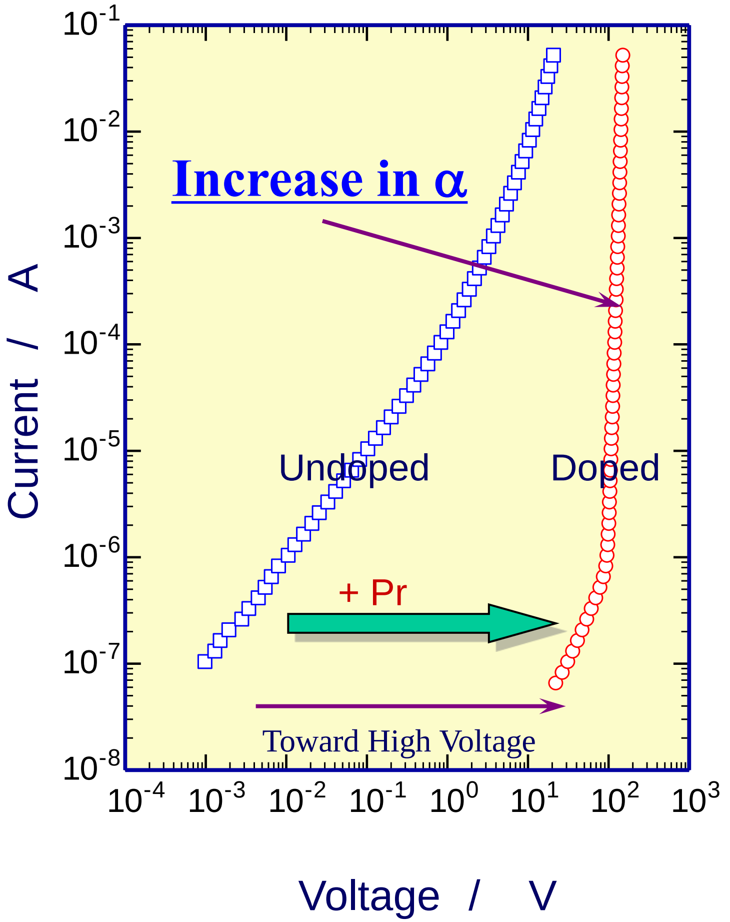
Varistor (ZnO)

Device to protect from static electricity and mechanical shock

Electro devices

～0.2mol%-Pr doping

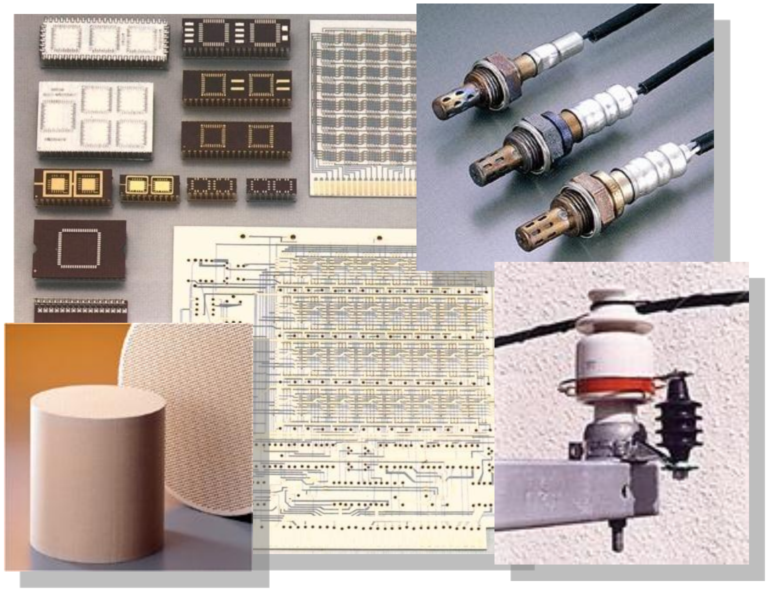
Great Improvement of Varistor Properties



Dopant Effect

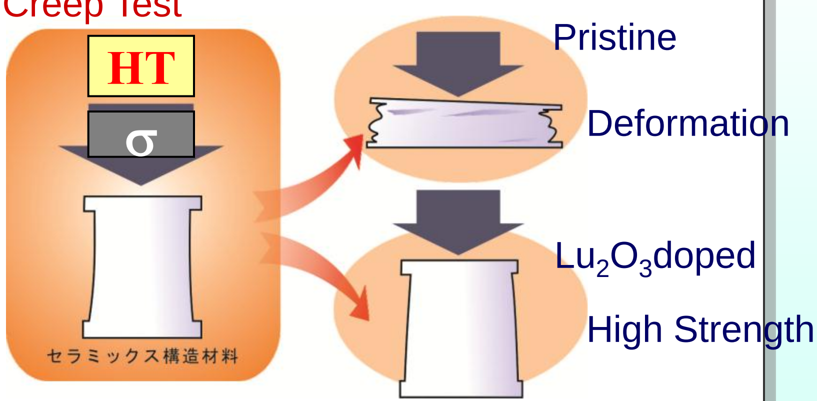
Alumina（Al_2O_3）

Structural Ceramics for IC chip substrate、Insulator、Catalyst carrier



High Temperature Ceramics

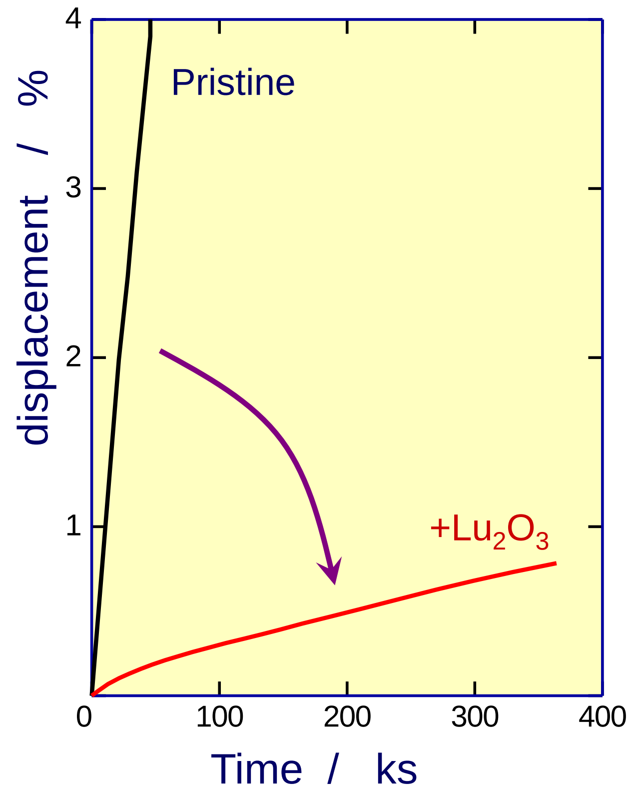
Creep Test

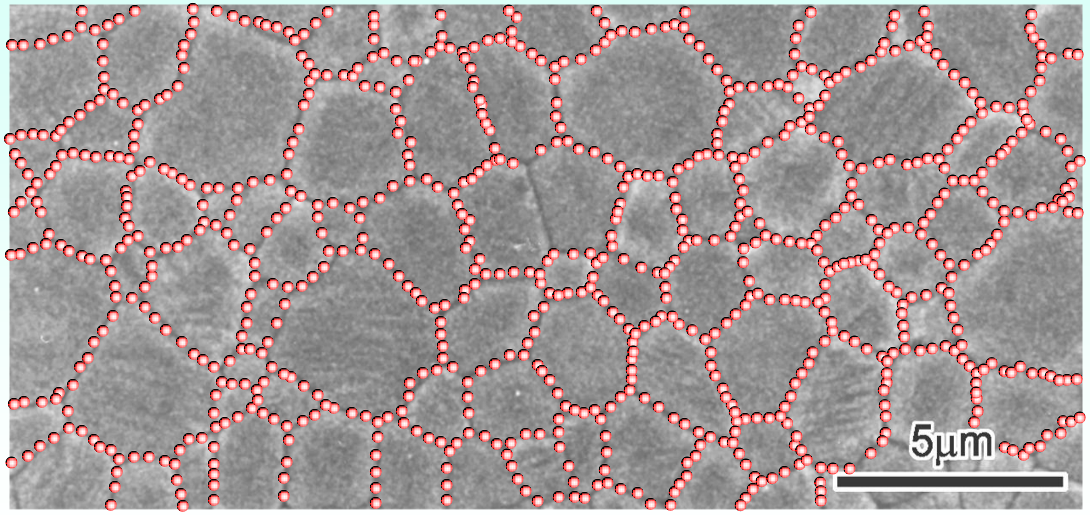


0.05mol% rare-earth doping

Improvement of Creep resistance by doping Lu_2O_3 (X100)

Creep Curve、1250℃、50MPa



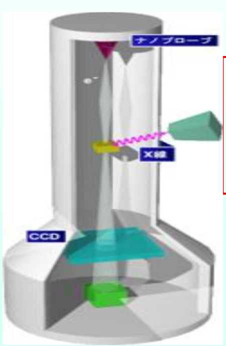


Grain Boundary Segregation

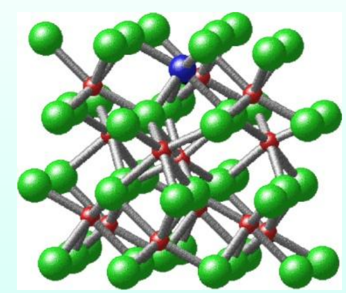
↓

Properties of Materials

GB Segregation Behavior



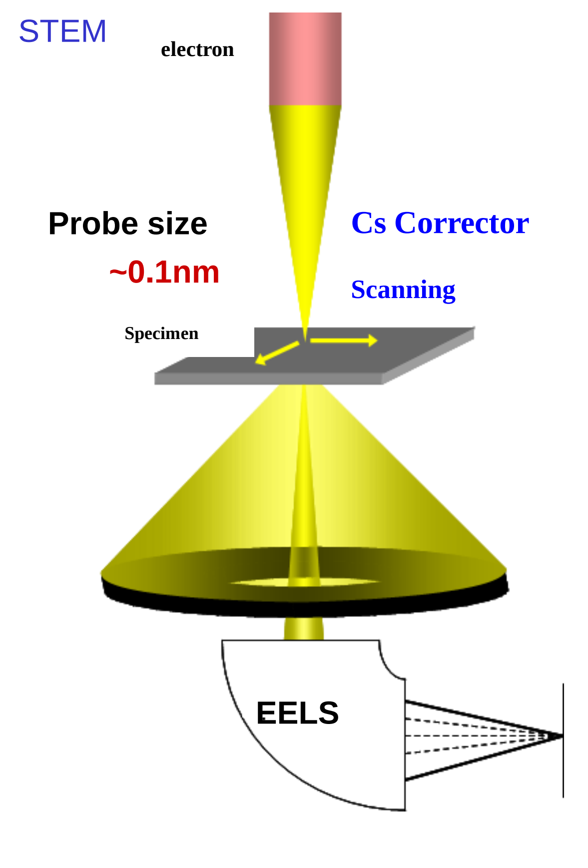
Atomic Characterization ⟷ **Theoretical Calculation**



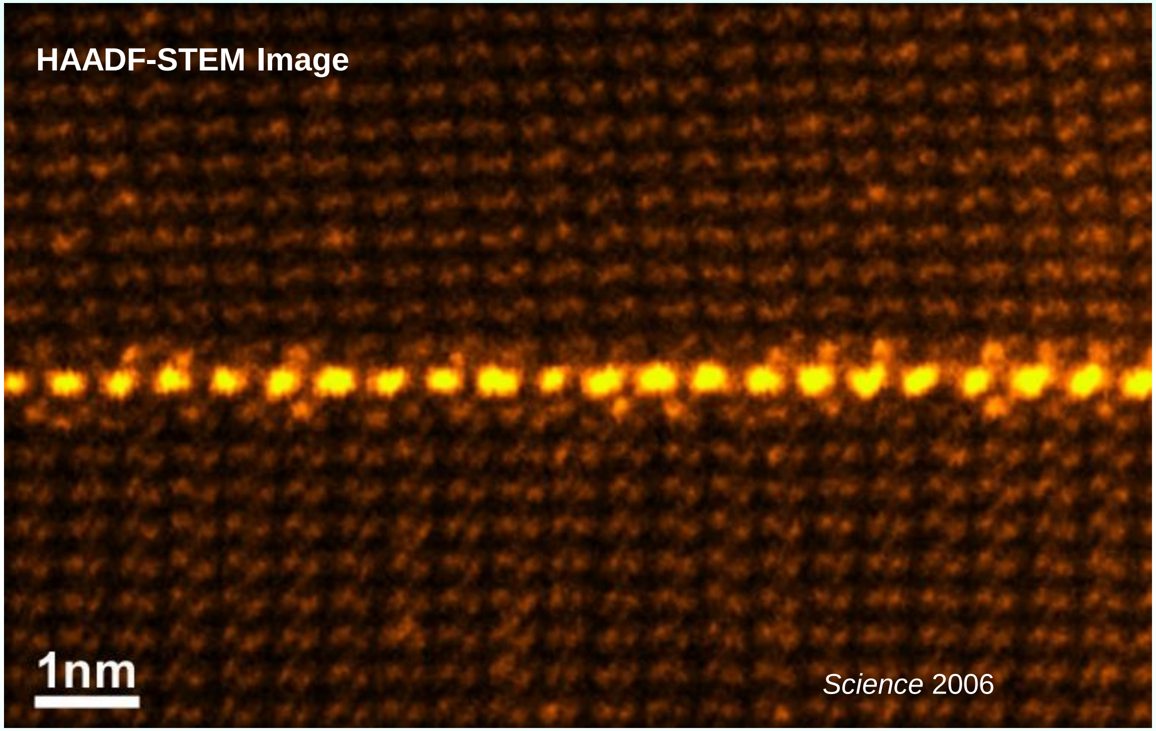
Atomic Structure around GB including dopants
Electronic Structure which is related to Properties

Breakthrough in Electrom Microscopy (Cs corrected STEM)

HAADF-STEM (High Angle Annular Dark Field-STEM)
(Z-Contrast Imaging)



Lu_2O_3-doped Al_2O_3



Direct Observation of Segregated Dopant

$$I \propto Z^2$$

JEM-ARM200F

Specification

Item	JEM-ARM200F	Note
Acc.Voltage	120,200kV	
Resolution		
TEM		
Point	0.11nm	Cs Corected
Lattice	0.10nm	
Information Limit	0.10nm	
STEM		
DF-Image	0.08nm	Cs Corected
BF-Image	0.14nm	
Power Stability		
Acc.Voltage	1×10^{-6}/min	
OL Current	5×10^{-7}/min	

STEM-Theoretical Calculation-Materials Design

(1)Segregated Dopants at Ceramic Grain Boundaries

- Single dopant (Al_2O_3 : Y^{3+})
- Co-dopant (Al_2O_3 : Ca^{2+}+Si^{4+})
- Functional materials (ZnO: Pr)

(2)Catalyst (Au-nanoparticle on TiO_2)

(3) STEM Annular Bright Field Imaging

Direct Observation of Li Ions and H

($LiMn_2O_4$, $LiCoO_2$,VH_2)

STEM Characterization

JEOL 2100F with Cs corrector

ARM 200

STEM-Theoretical Calculation-Materials Design

(1)Segregated Dopants at Ceramic Grain Boundaries

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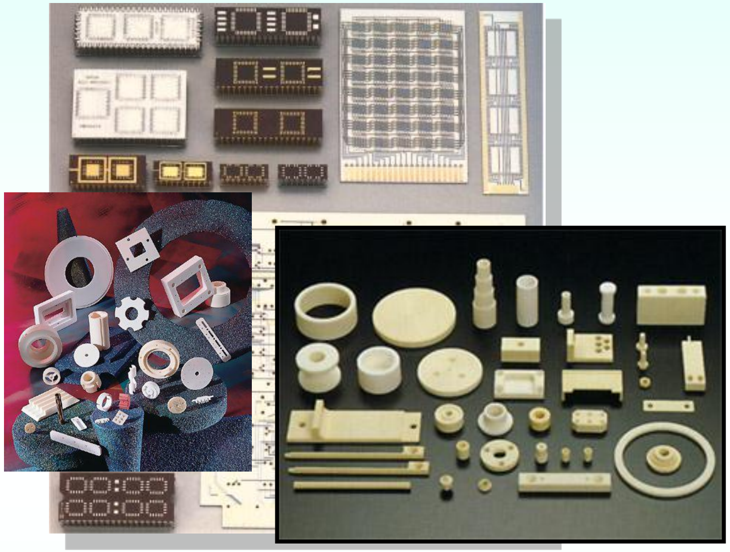
Introduction

α-Al_2O_3 Ceramics

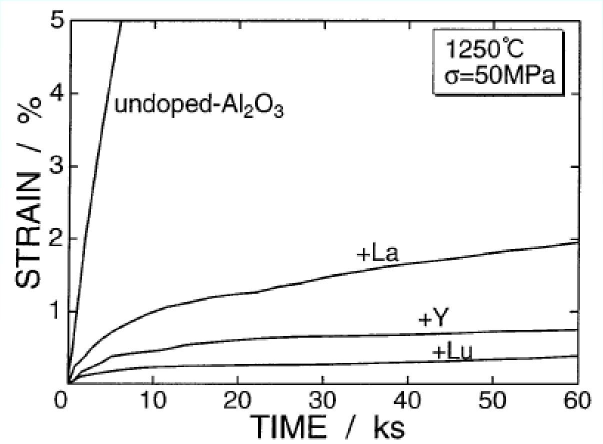


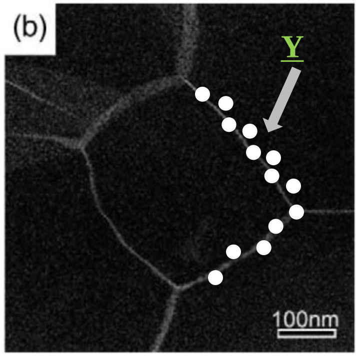
http://www.asuzac-ceramics.jp/material/material1.htm

High temperature structural materials

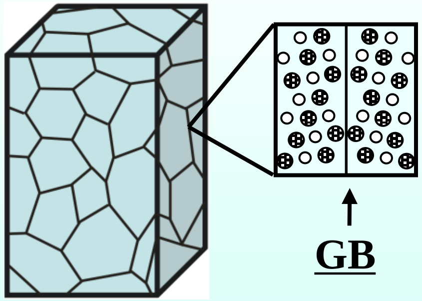
→ High temperature properties

High temperature properties of α-Al_2O_3





Yoshida, H. et.al., *J. Mater. Res.*, (1997)

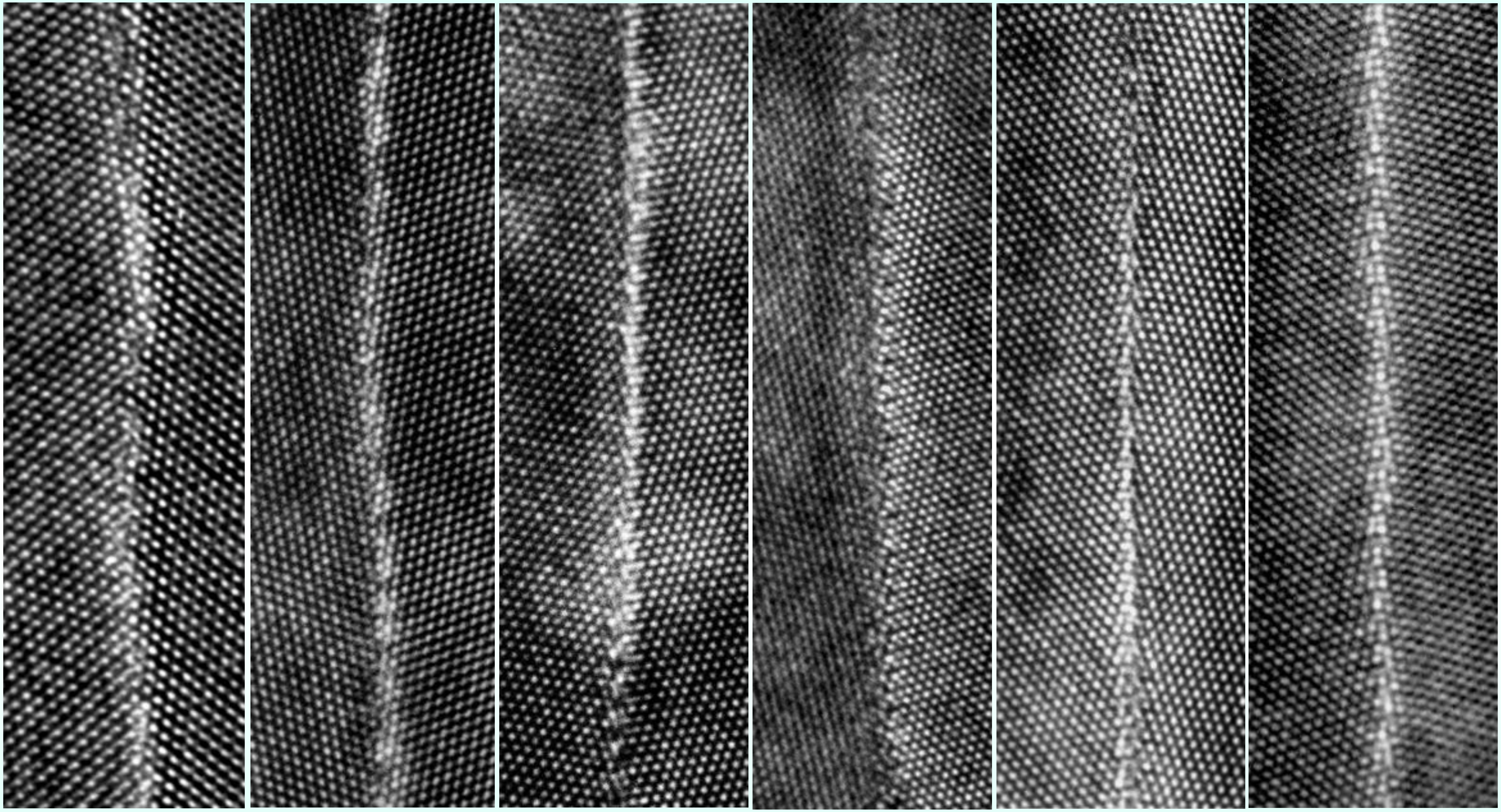


G.B.- segregated dopants enhance the high temperature creep resistance

⇓

Atomic scale understanding of G.B. segregation is important

Various types of Grain Boundaries



$\Sigma 31/\ \{71\overline{14}0\}$ $\Sigma 21/\ \{23\bar{1}0\}$ $\Sigma 7/\ \{45\bar{1}0\}$ $\Sigma 13/\ \{57\bar{2}0\}$ $\Sigma 21/\ \{45\bar{1}0\}$ $\Sigma 7/\ \{23\bar{1}0\}$

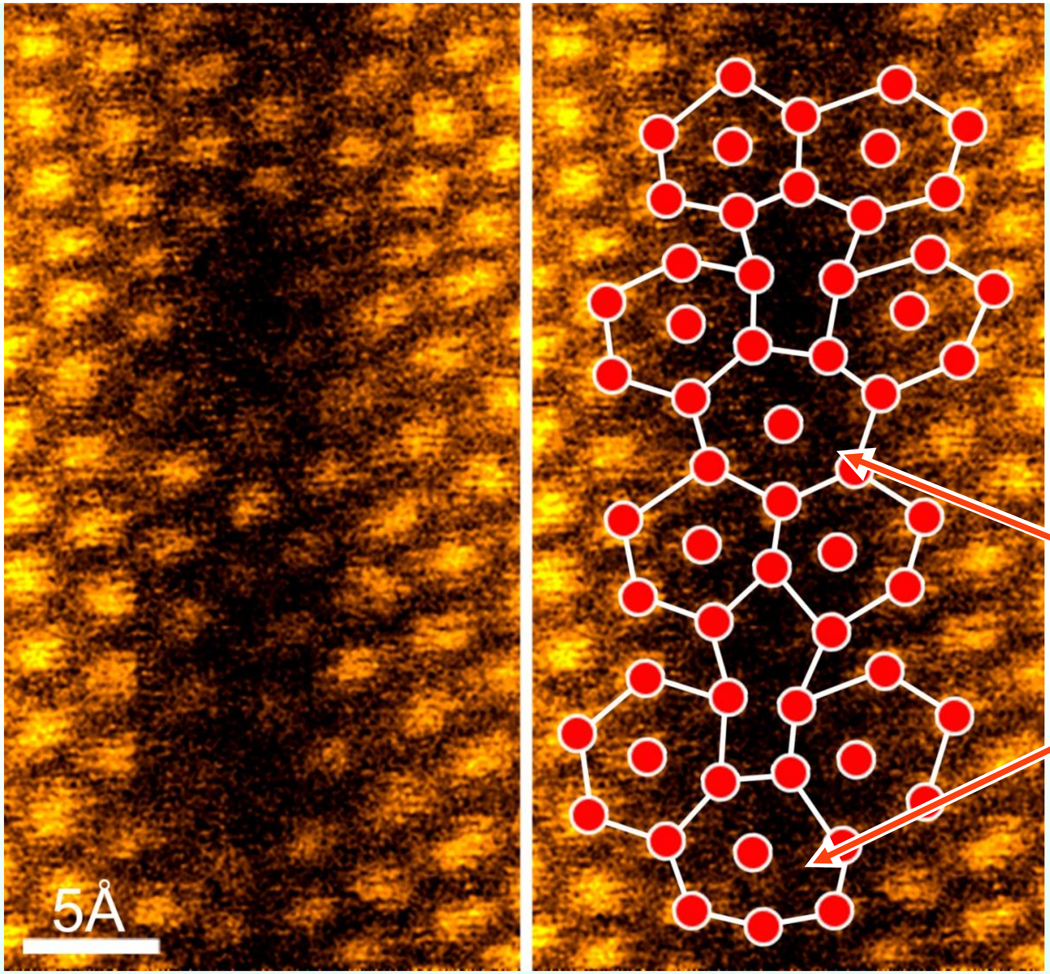
⊙ [0001]

2 nm

HAADF-STEM Image of Alumina Σ31 Grain Boundary

JEOL2100F
U.Tokyo

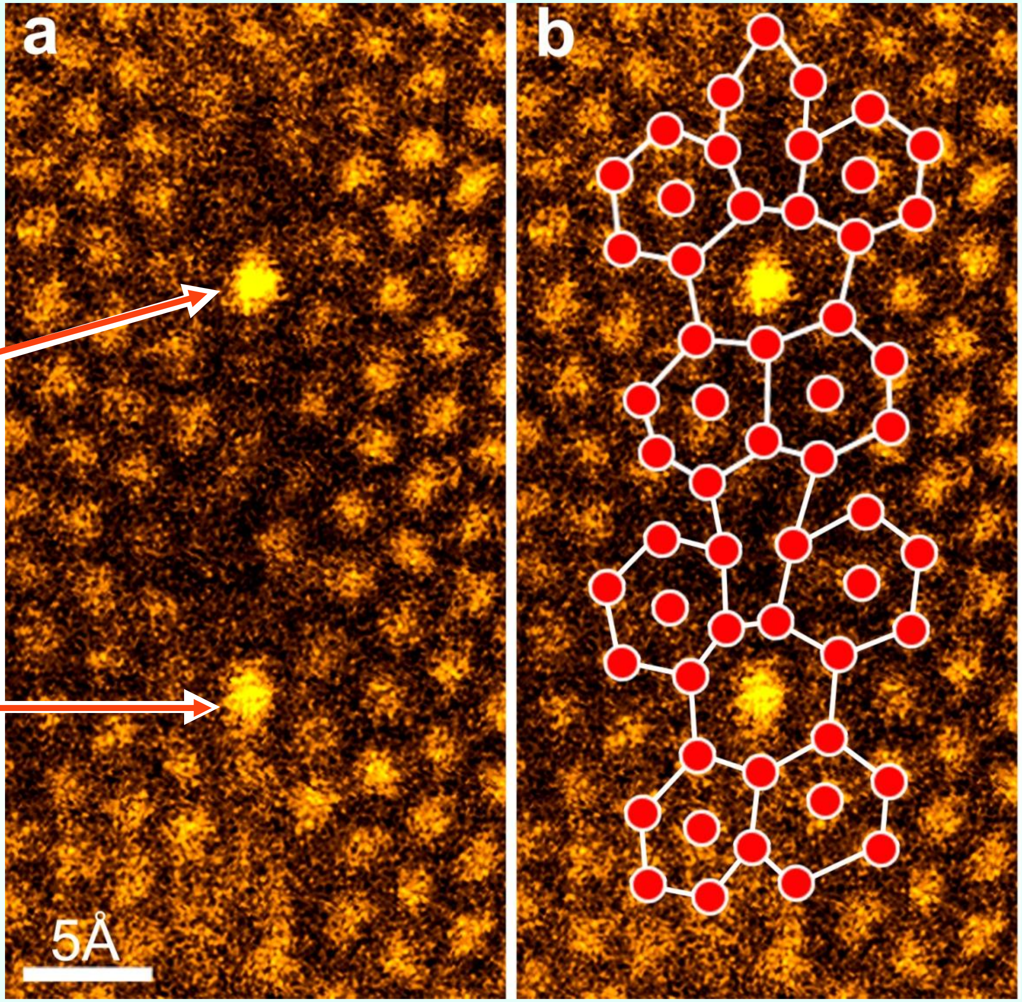
Al_2O_3



The Al cation sublattice atomic structure is revealed in the STEM image, showing the presence of 7-membered ring structures.

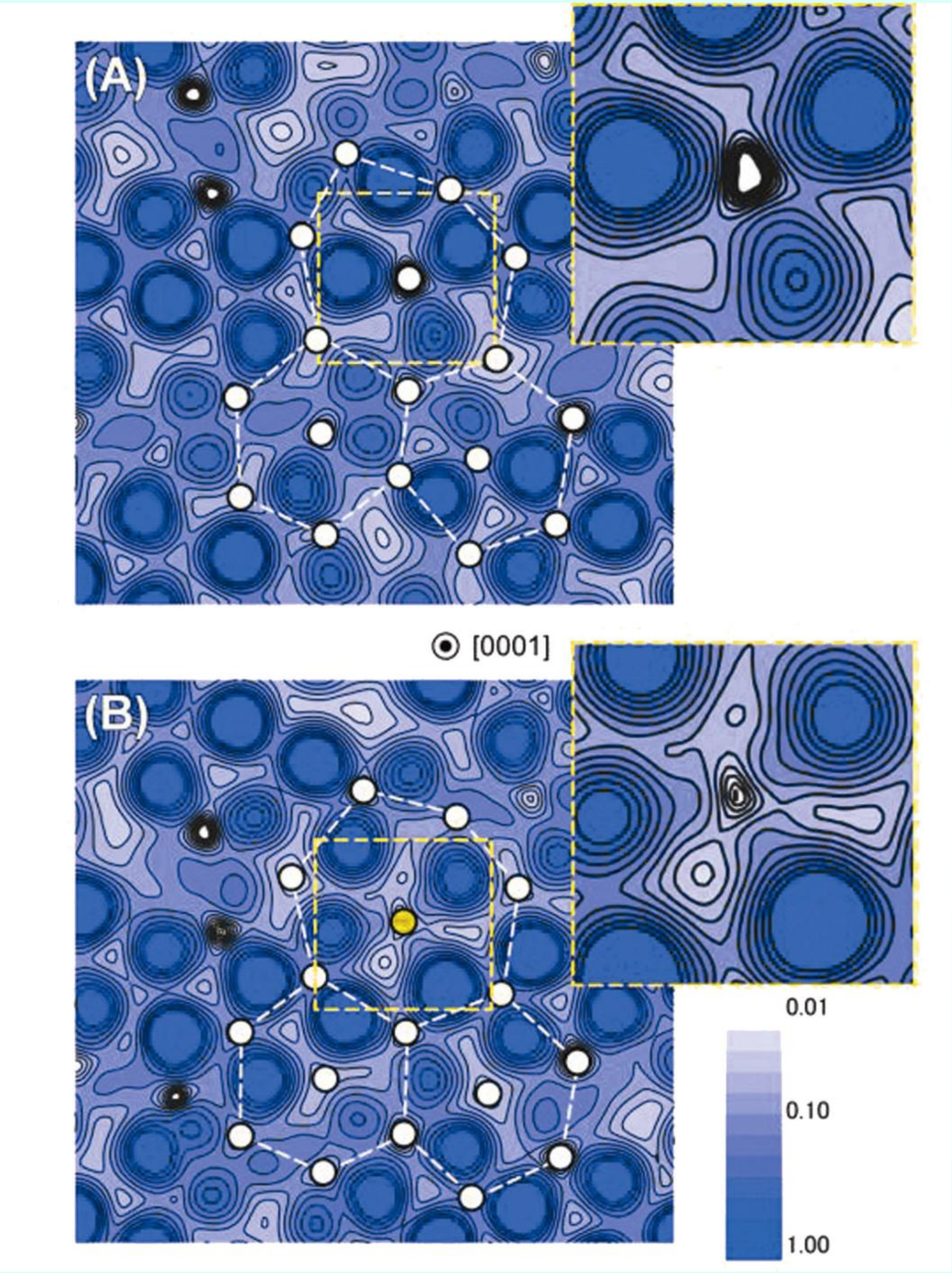
HAADF-STEM Image of the Σ31 Y-doped Boundary

Y appears very bright in the Z-contrast image



Science (2006)

The basic grain boundary structure is relatively unaltered in comparison to the undoped case.The location of the Y ions are revealed by the STEM image

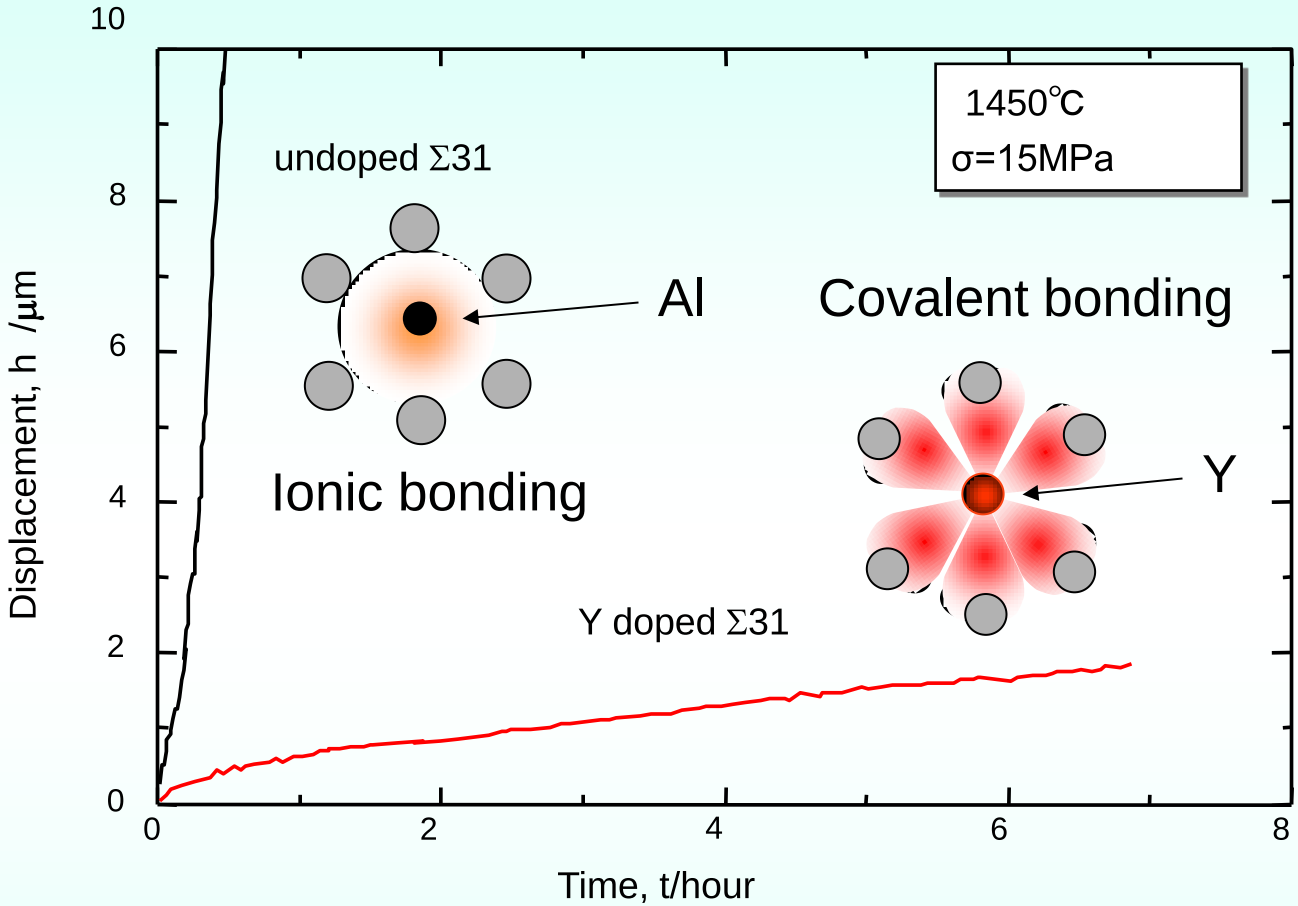


Pristine GB
Ionic Bonding

Y-doped GB
Covalent Bonding

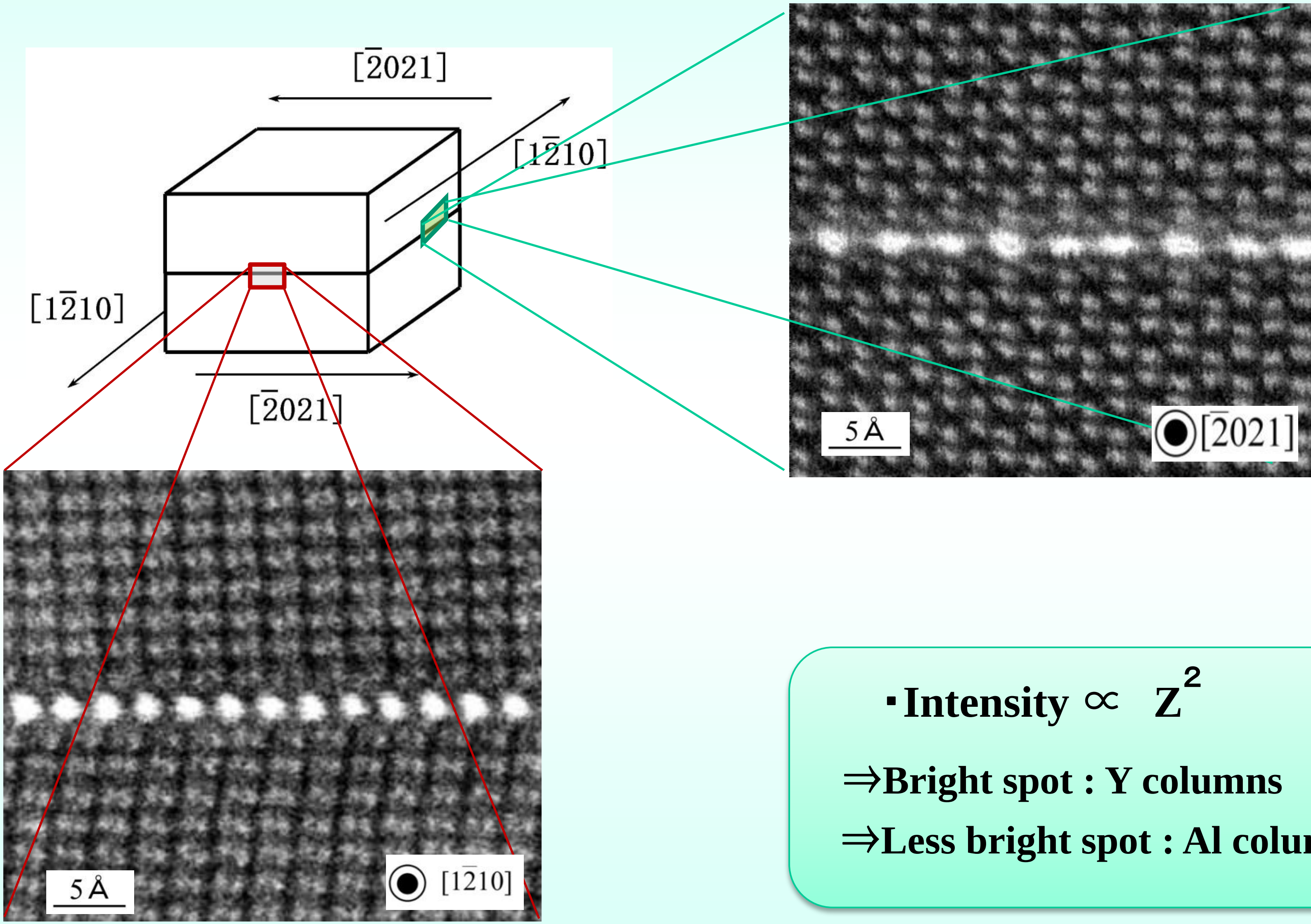
Science (2006)

Model for Creep Resistance Due to Doping



The presence of Y has been shown to increase the covalency (and strength of the cation-anion bonds) in alumina GB

HAADF-STEM images of Y doped Σ13 grain boundary

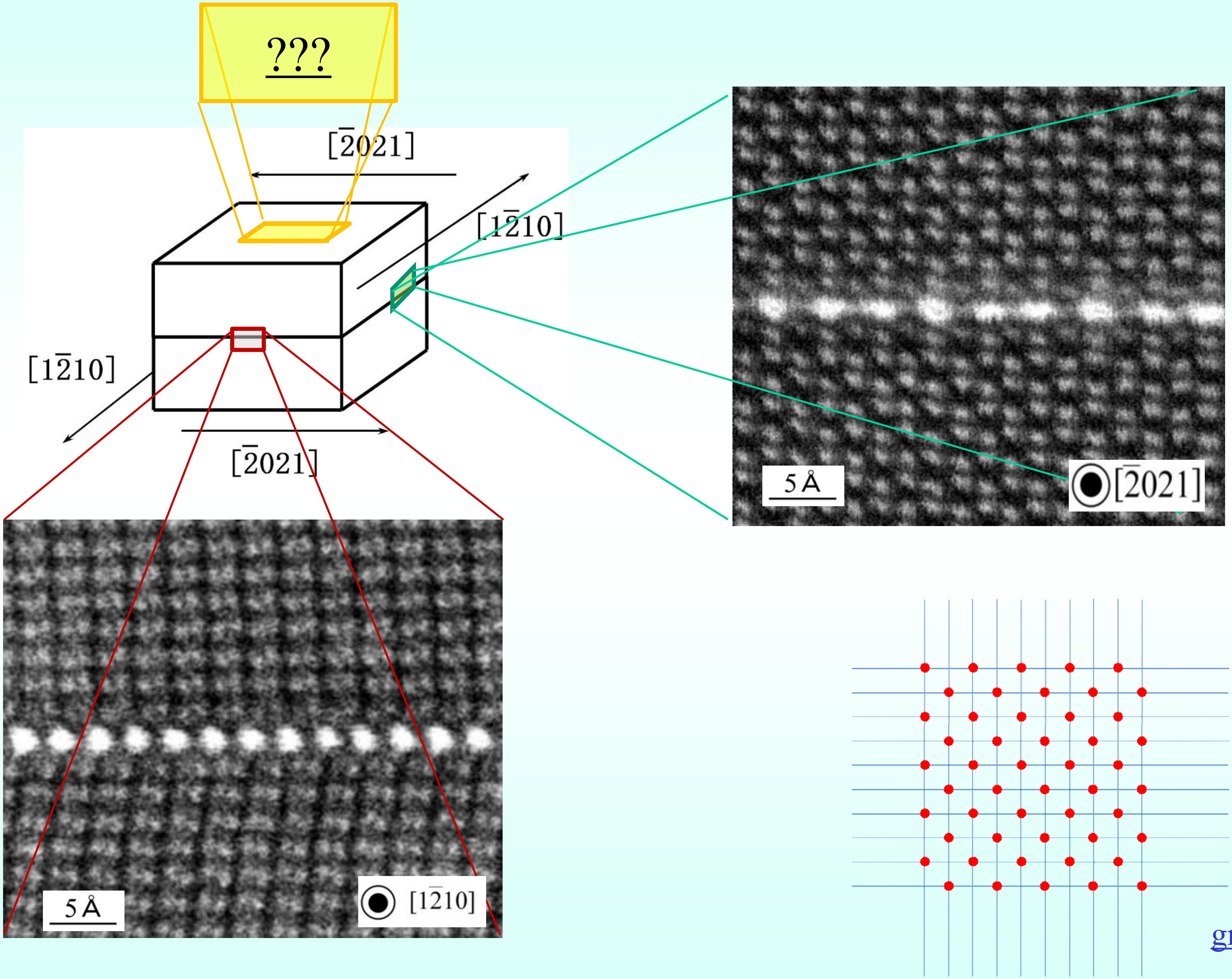


- Intensity $\propto$ Z^2

⇒Bright spot : Y columns

⇒Less bright spot : Al columns

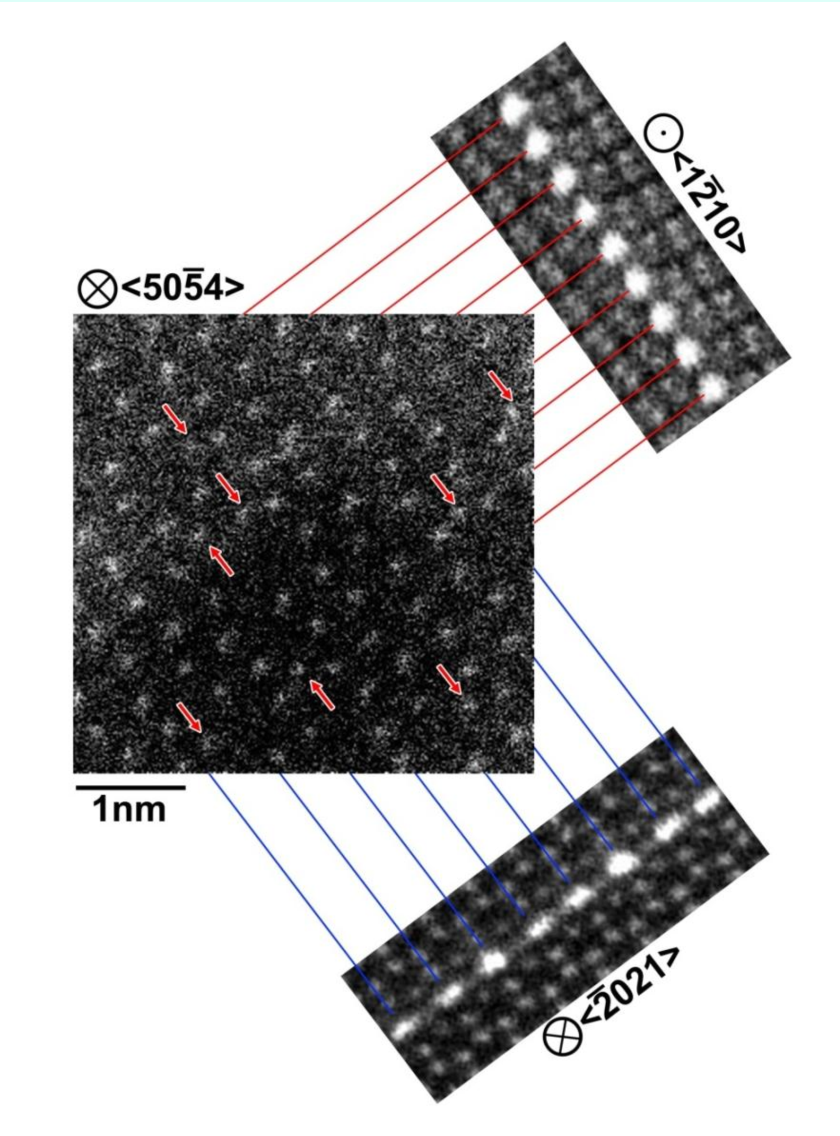
Plan-view imaging

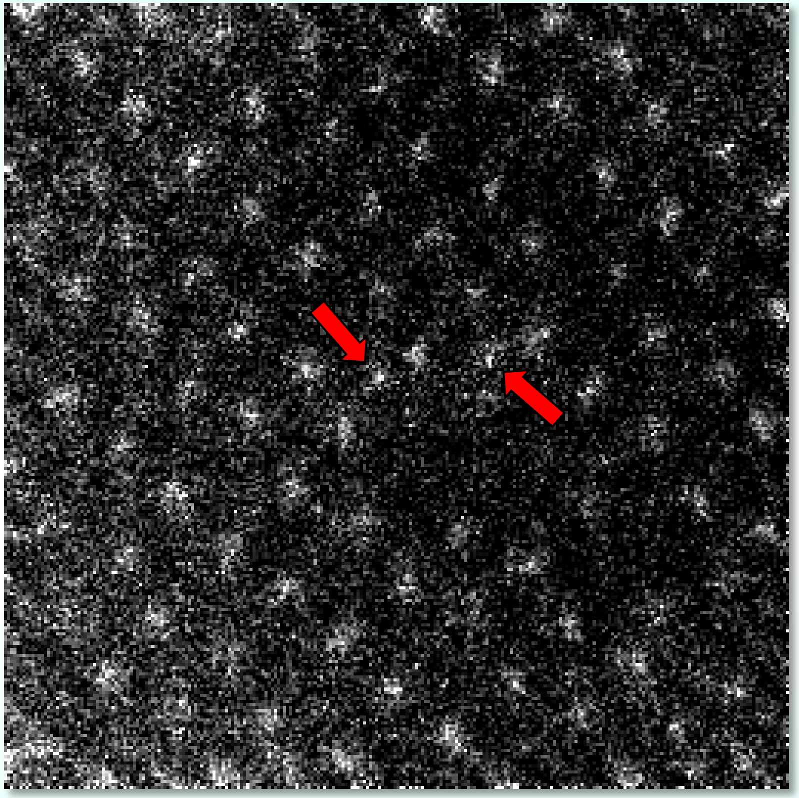


grid

Nature Materials, 8, 654 (2009)

Local disordering at the interface!





Disordering at a single atom level can be detected!

STEM plan-view imaging directly highlights individual dopant atoms in a buried interface!

STEM-Theoretical Calculation-Materials Design

(1)Segregated Dopants at Ceramic Grain Boundaries

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- Co-dopant (Al_2O_3 : $Ca^{2+}+Si^{4+}$)
- Functional materials (ZnO: Pr)

(2)Catalyst (Au-nanoparticle on TiO_2)

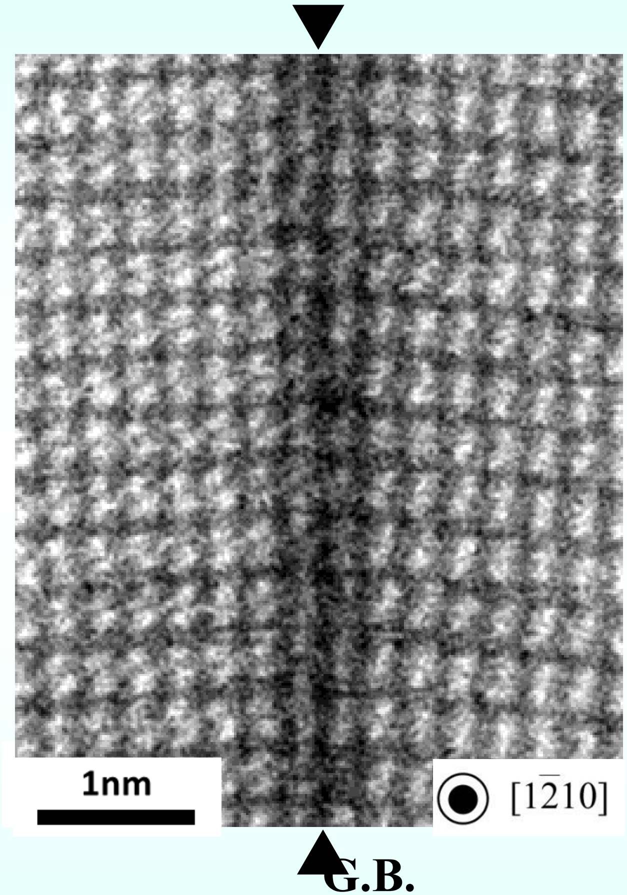
(3) STEM Annular Bright Field Imaging

Direct Observation of Li Ions and H

($LiMn_2O_4$, $LiCoO_2$, VH_2)

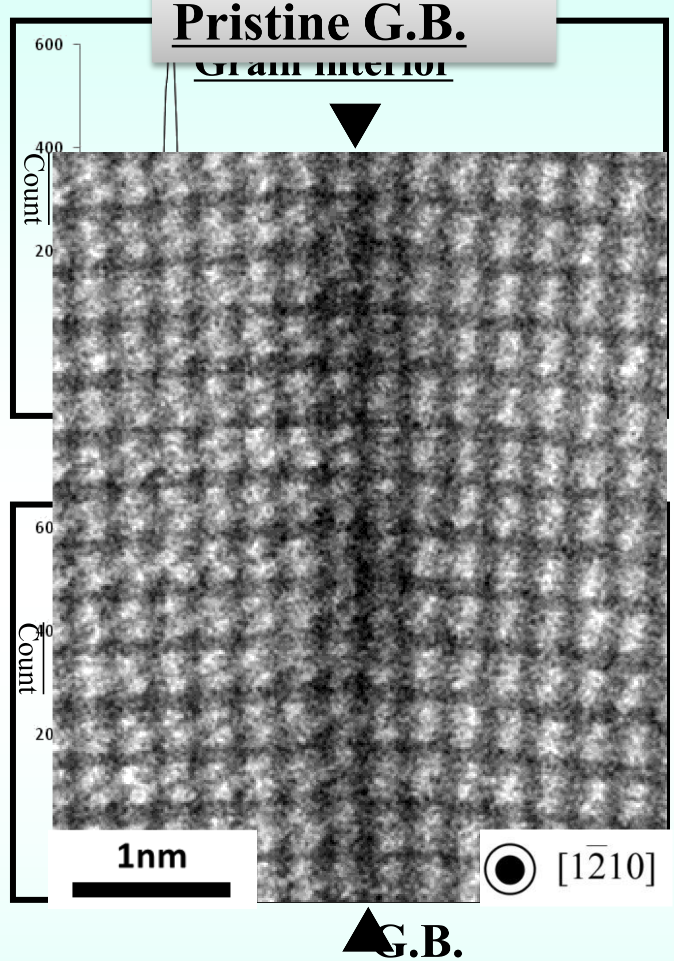
Al_2O_3: Ca-doped G.B.(Σ13)

Ca-doped G.B.



Bright spots were not observed

Pristine G.B.

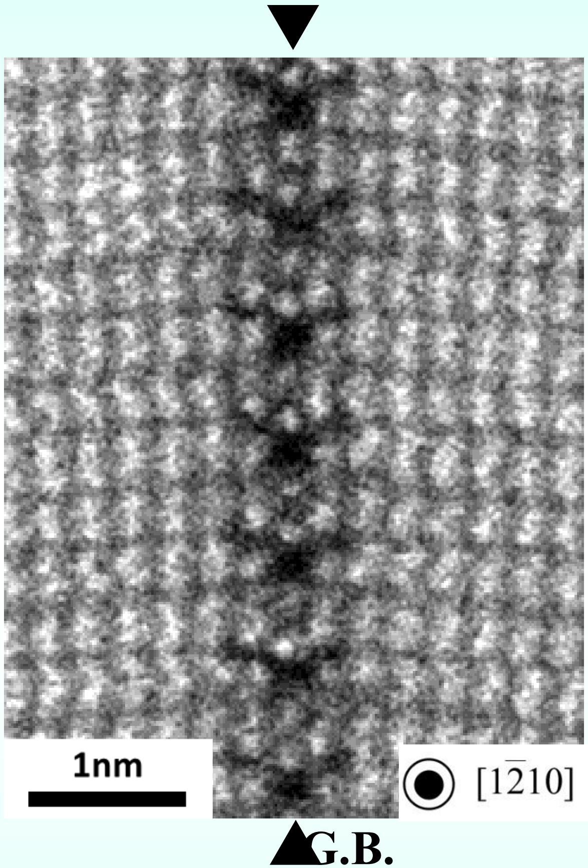


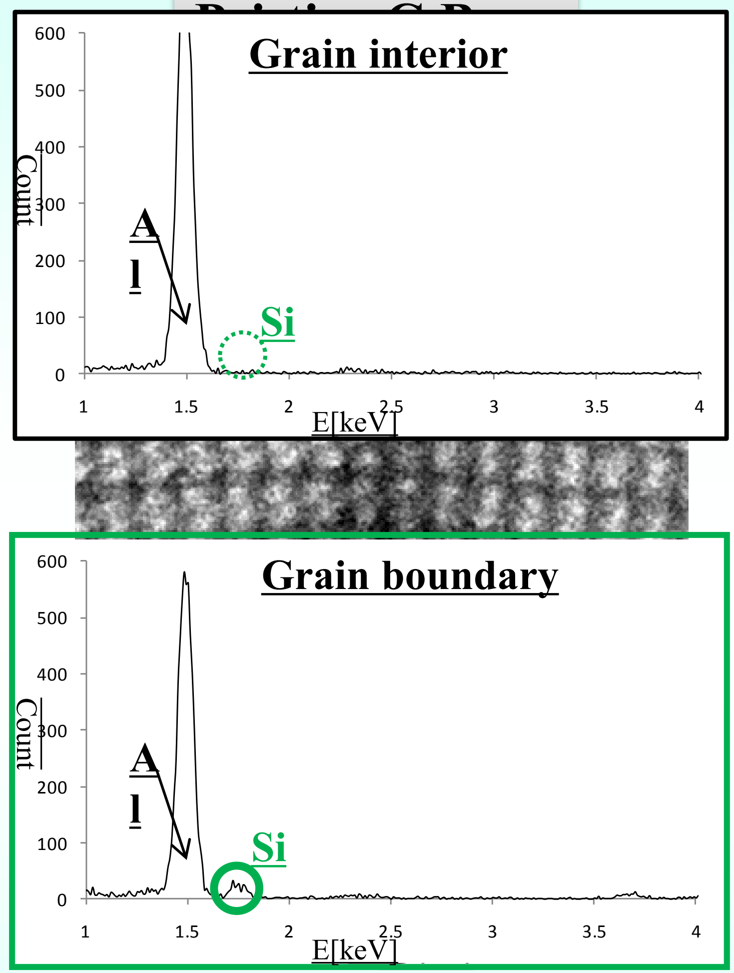
Ca atoms were not detected

Ca(Z=20) >> Al (Z=13) >> O (Z=8)

Al_2O_3: Si-doped G.B.

Si-doped G.B.





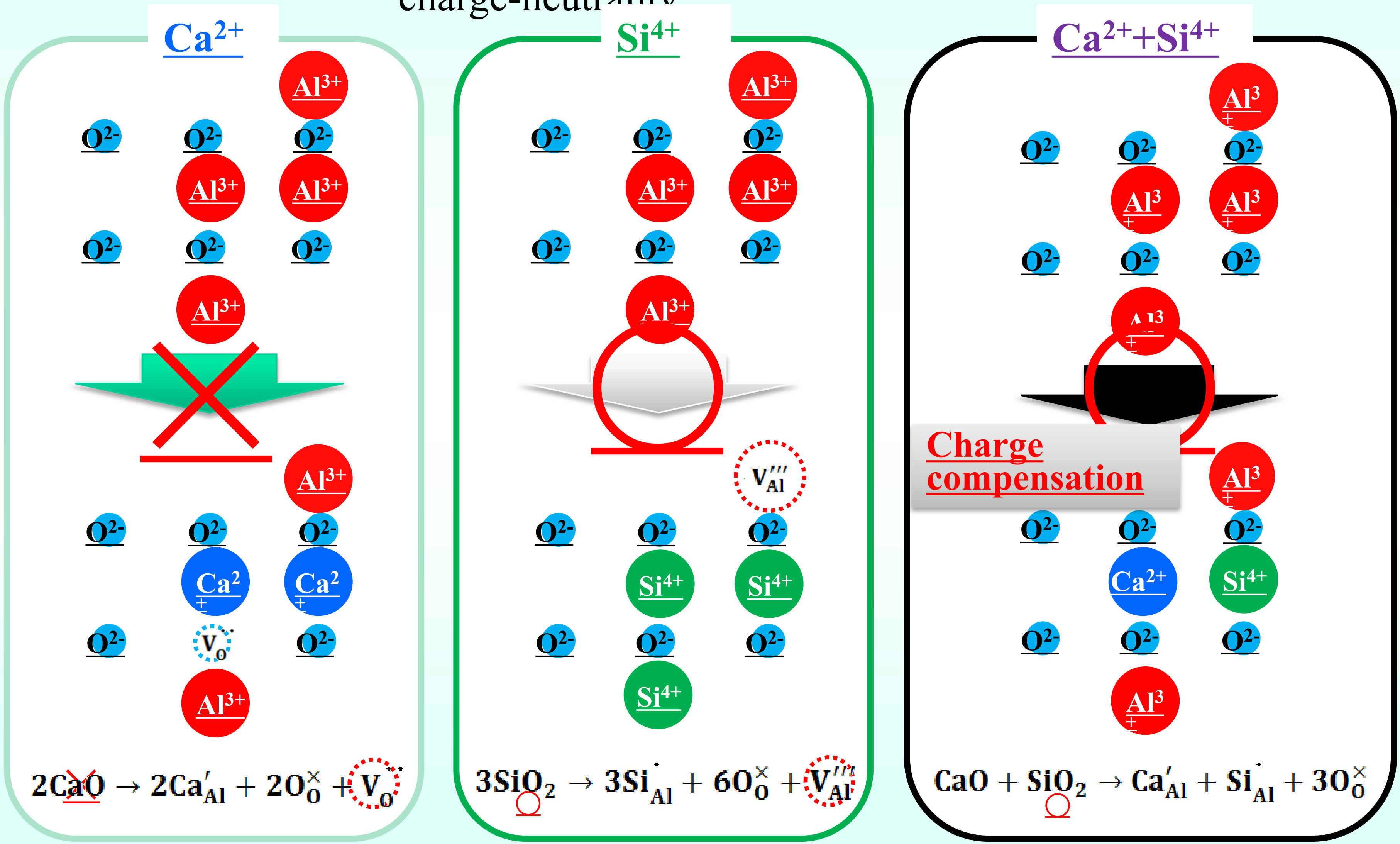
Different from pristine G.B.

Si atoms were detected

Si (Z=14) ≒ Al (Z=13) >> O (Z=8)

Charge Effect

To segregate Ca^{2+}/Si^{4+} and keep charge-neutrality



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Direct Observation of Li Ions and H

($LiMn_2O_4$, $LiCoO_2$,VH_2)

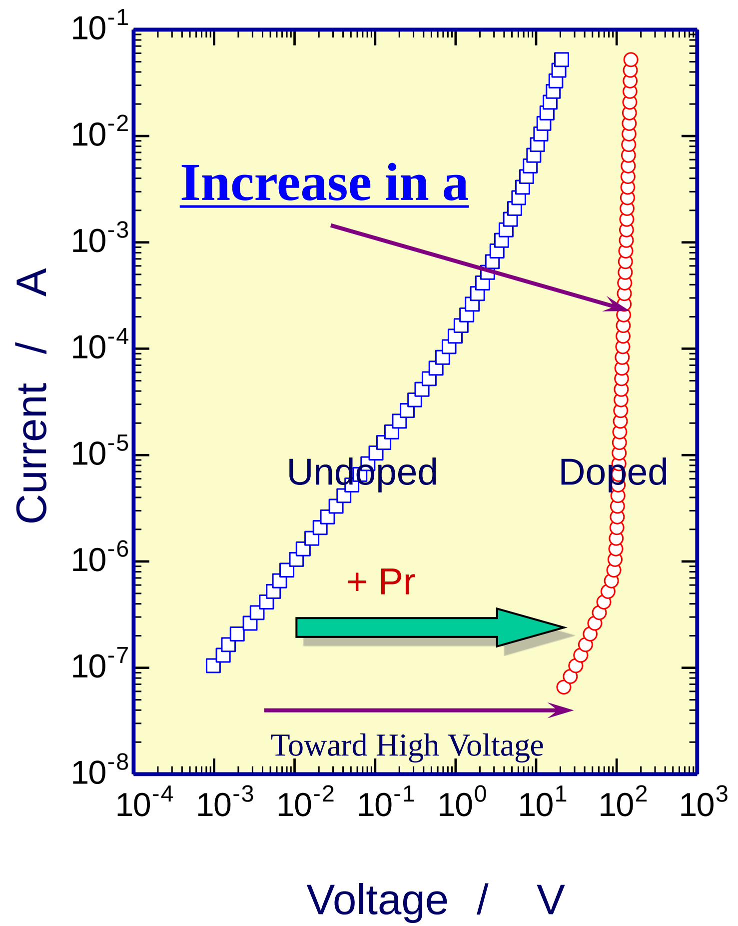
Varistor (ZnO)

Device to protect from static electricity and mechanical shock

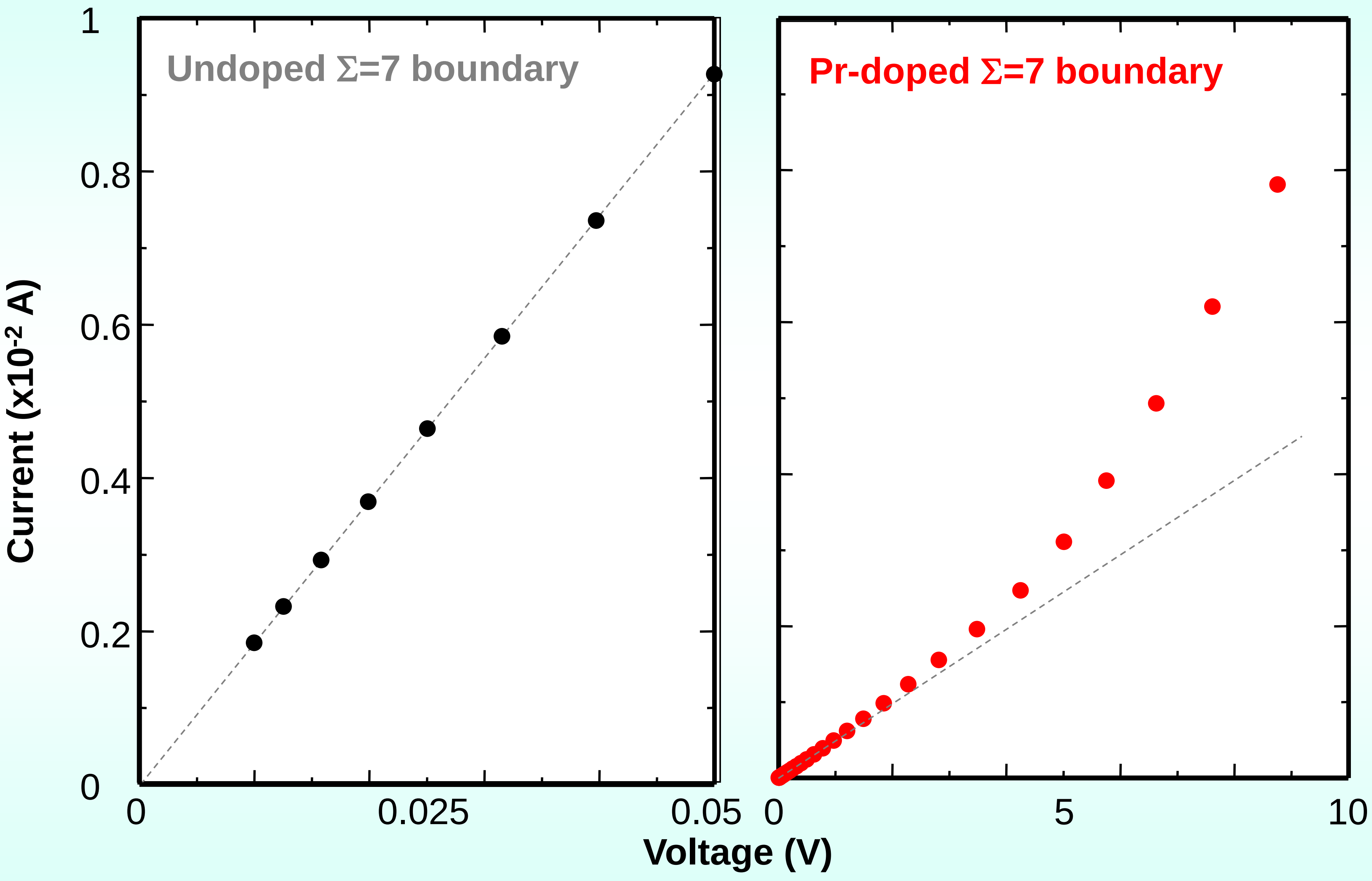
Protection device

~0.2mol%-Pr doping

Great Improvement of Varistor Properties

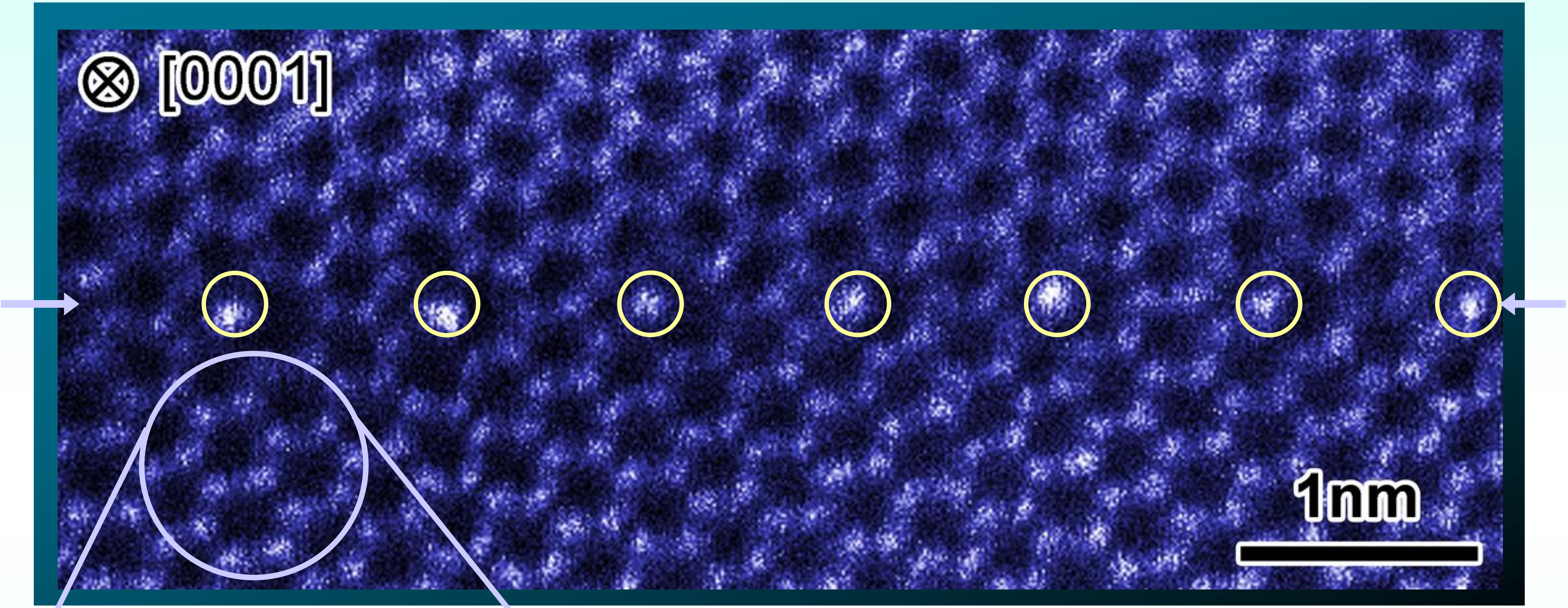


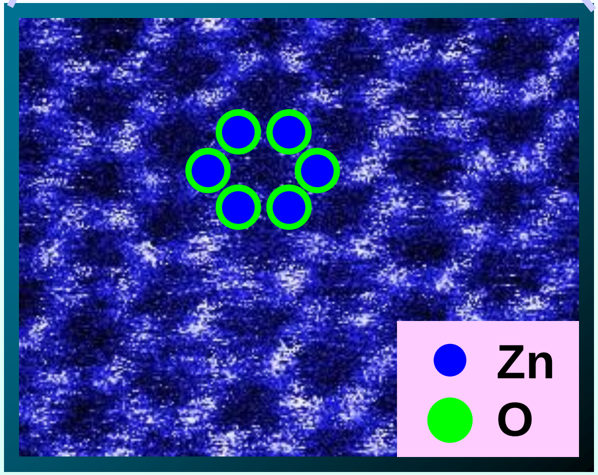
I-V characteristic of ZnO bicrystals



The nonlinear *I-V* characteristic results from the Pr.

HAADF-STEM image of the Pr-doped ZnO GB





- **Z-contrast imaging**

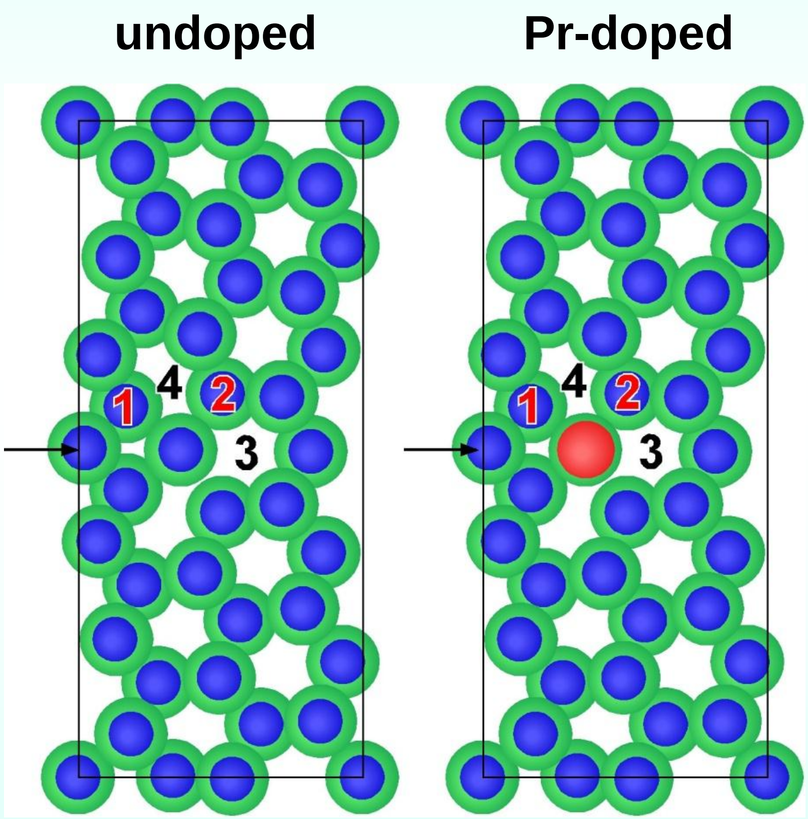
Heavier atoms (Pr: Z=59, cf. Z=30 for Zn) appear much brighter.

→ The Pr segregates to specific atomic columns of the boundary (no interfacial layers).

PRL (2006)

Formation energy of Zn vacancy (V_{Zn}) and O interstitial (O_i)

V_{Zn} at the site 1 and 2, O_i at 3 and 4 are calculated.

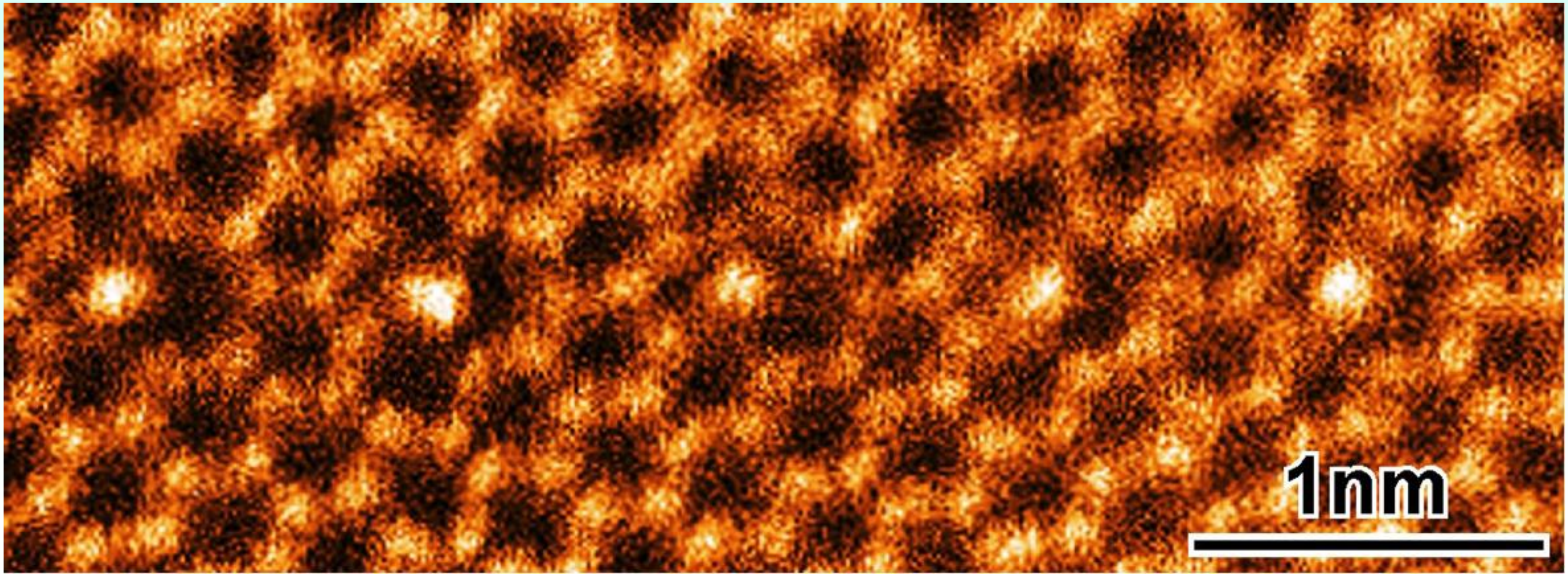


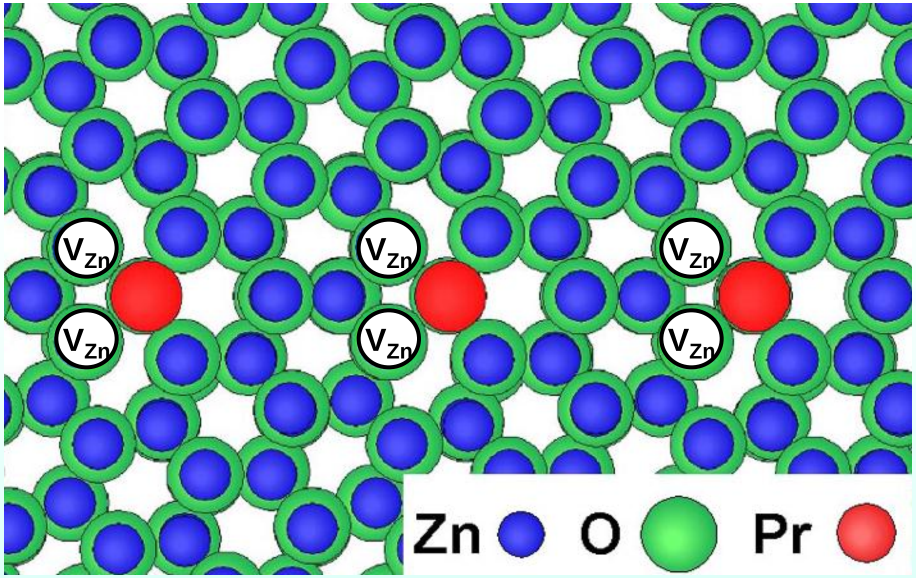
Defect formation energy

undoped (eV)		Pr-doped (eV)
0.4	1 (V_{Zn})	0.1
1.4	2 (V_{Zn})	0.7
3.2	3 (O_i)	1.5
3.2	4 (O_i)	2.2

V_{Zn} is more stable than O_i.
Pr-doping lowers the formation energies.

Pr promotes the formation of native defects. (particularly V_{Zn})





STEM+First Principle

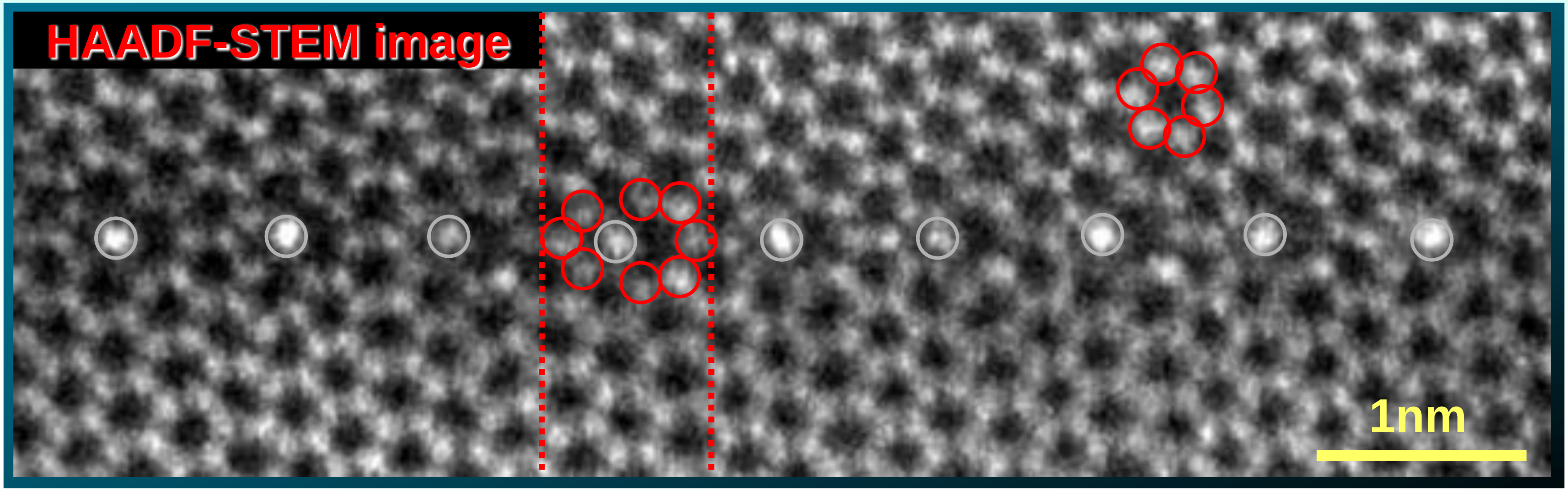
Origin of Varistor Properties

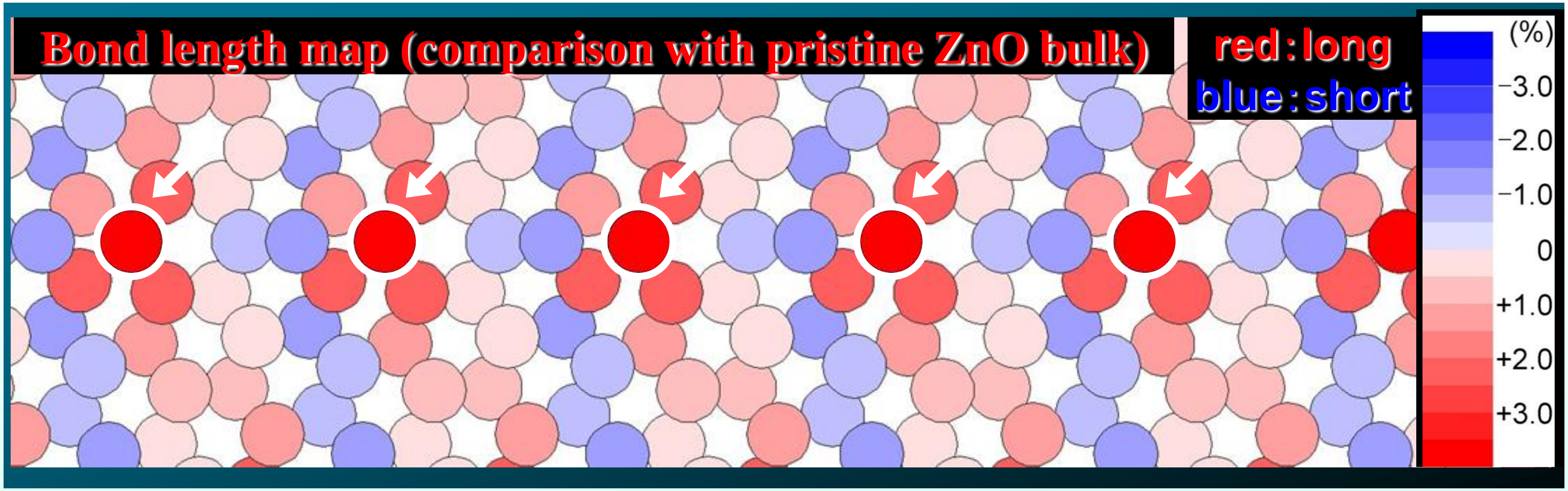
High Performance Varistor

The role of Pr can be understood by First Principles calculation

PRL (2006)

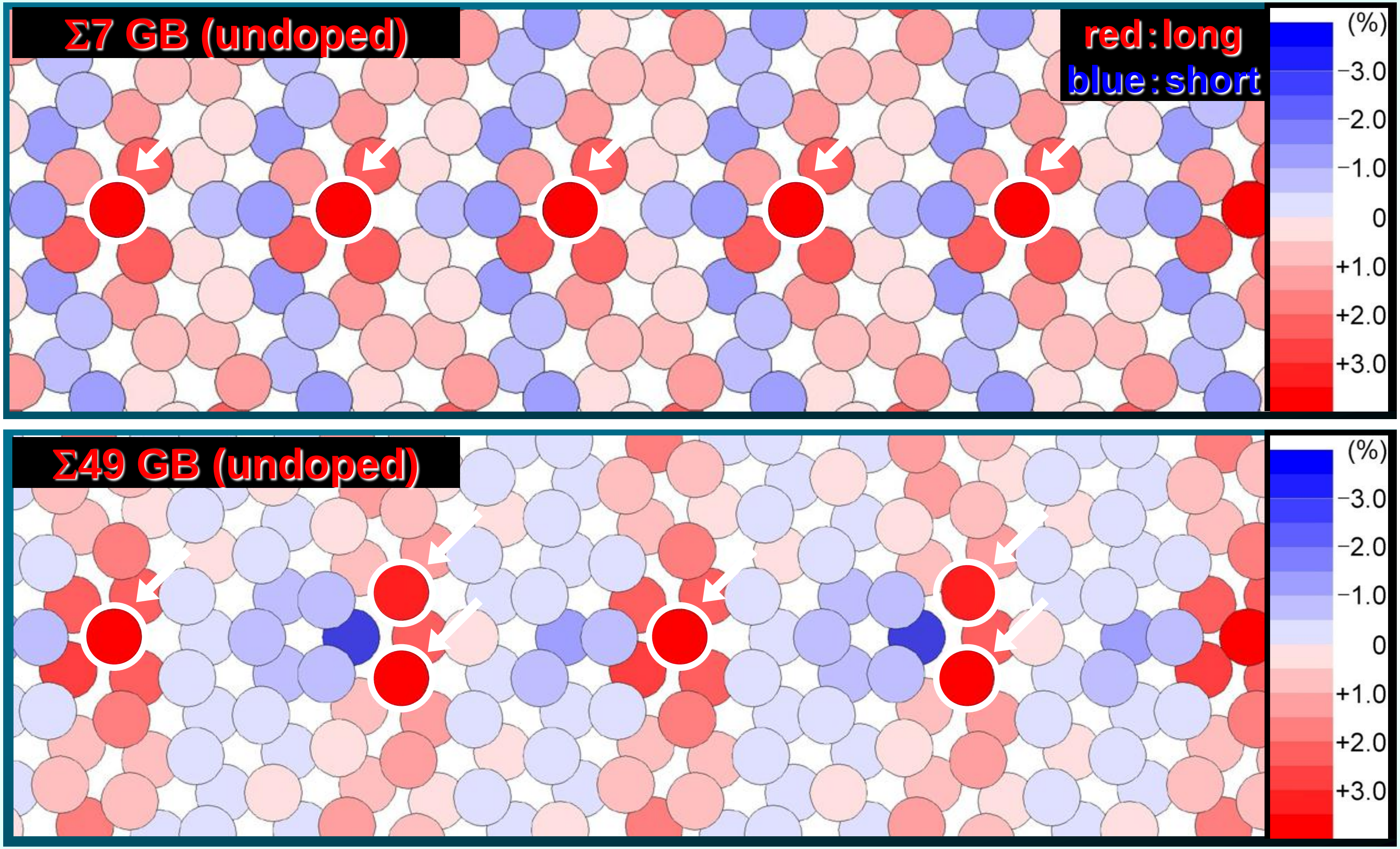
Factor to determine the segregation site; Pr-doped ZnO Σ7 GB





Pr segregates at the sites of the locally longest inter-atomic distance.

Bond length map (comparison with ZnO bulk)



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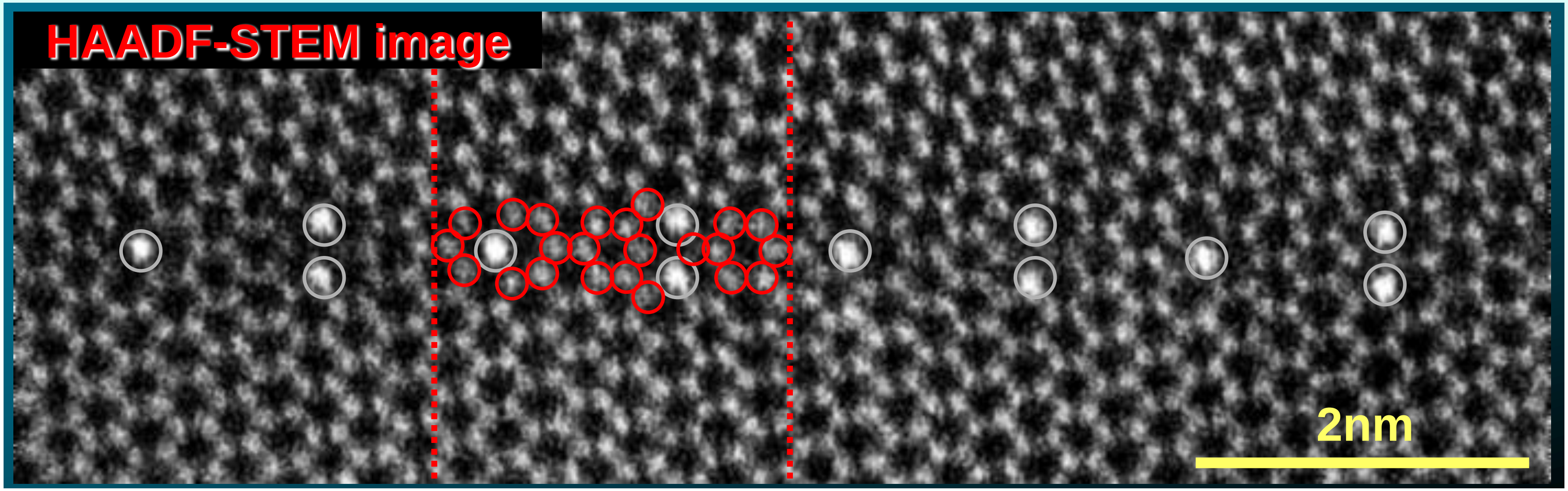

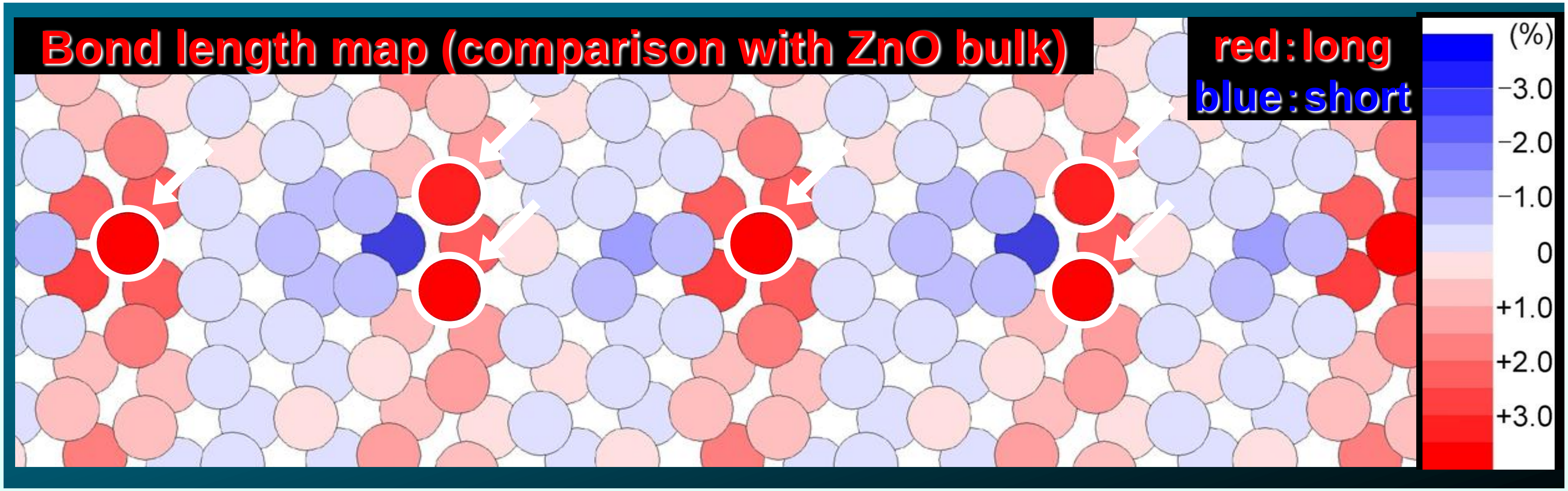

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PRB (2010)

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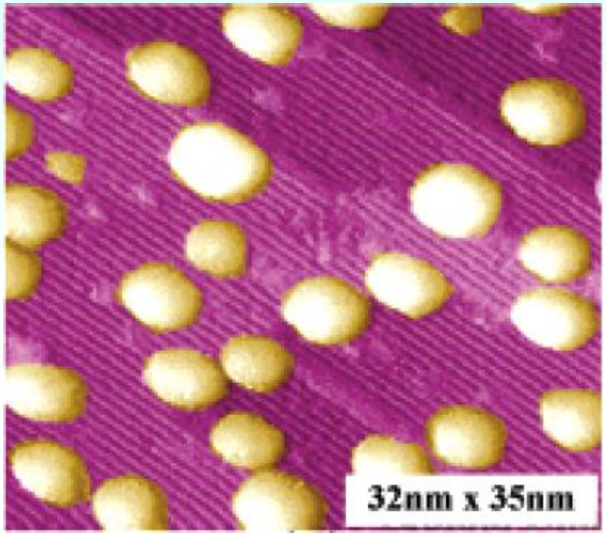
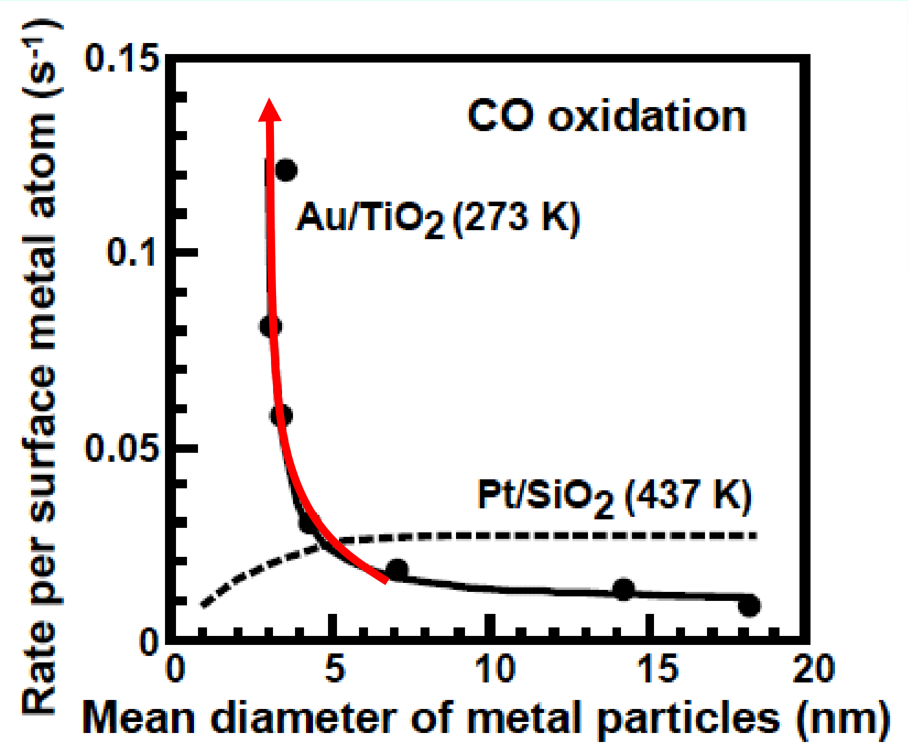
Nano hetero interface — Nanosized Au particles on TiO_2



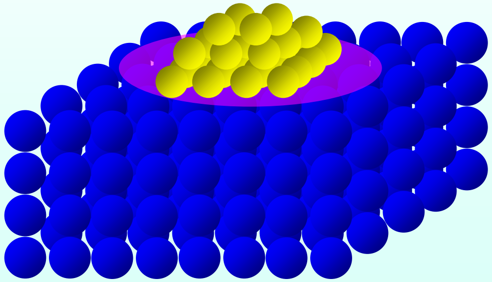
STM image of Au nanoparticles onTiO_2 surface

M. Valden, X. Lai and D.W. Goodman, Science (1998)



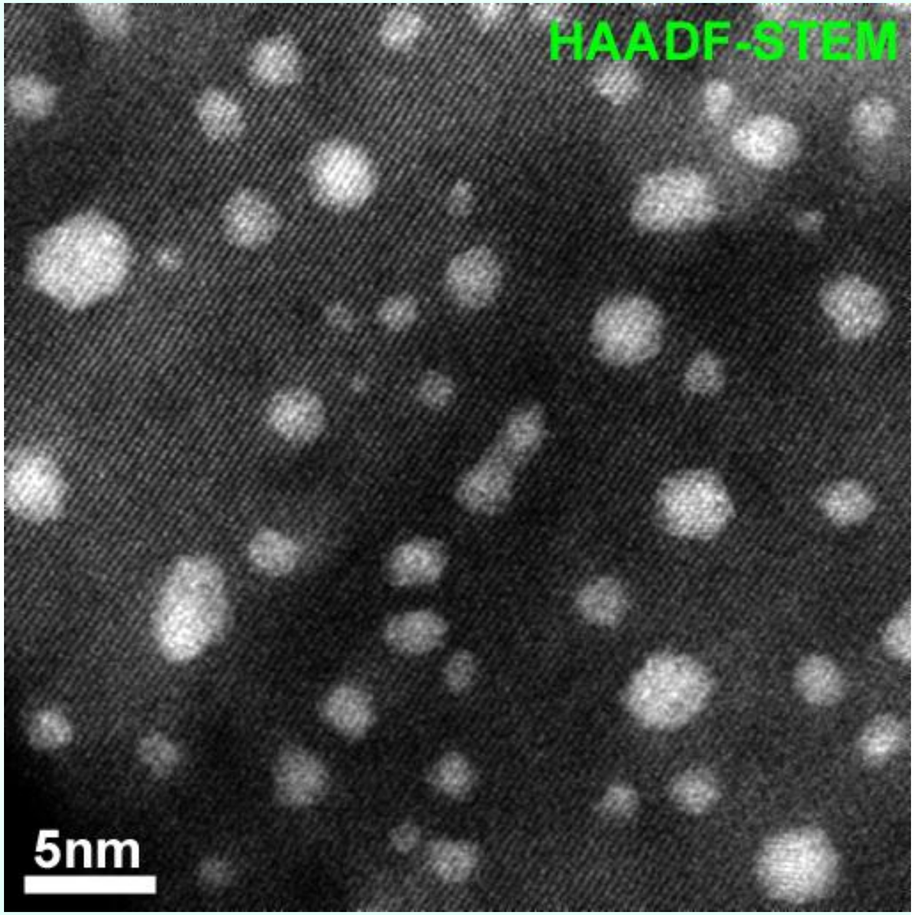
Au size effect on CO oxidation

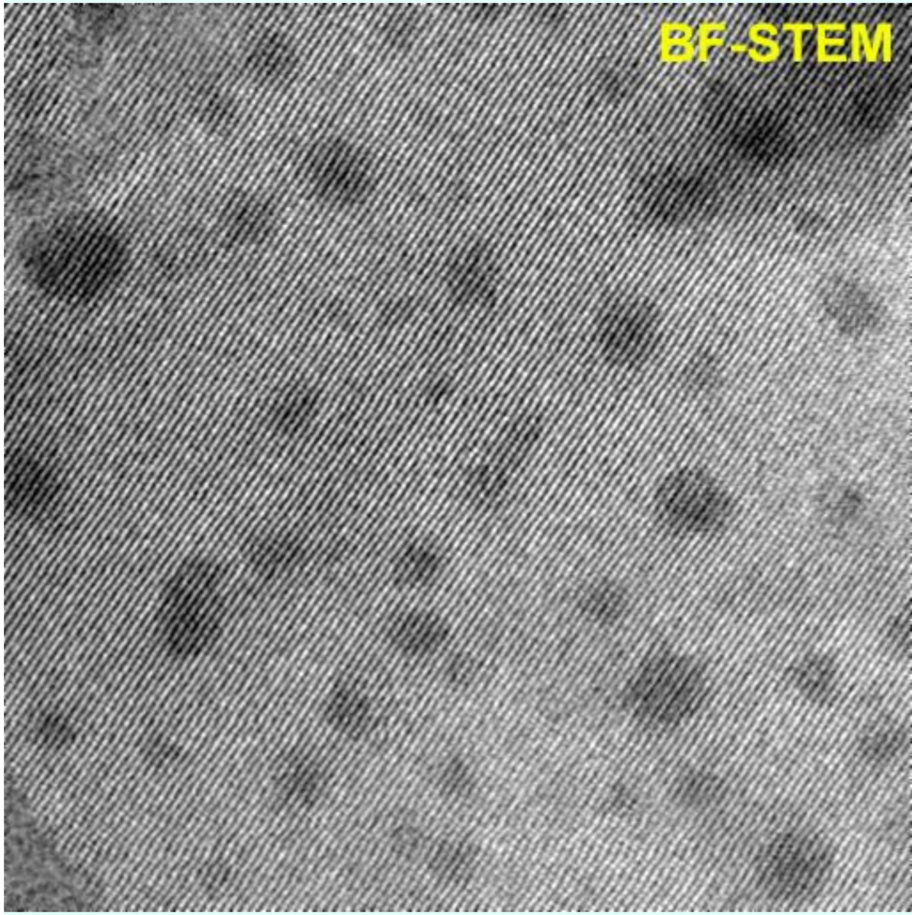
M. Haruta et al., J. Catal. (1993)



"Interfacial interaction" at nano-scale hetero interface is a key factor!

Comparison between HAADF-STEM and BF-STEM images of Au nanoparticles on TiO_2

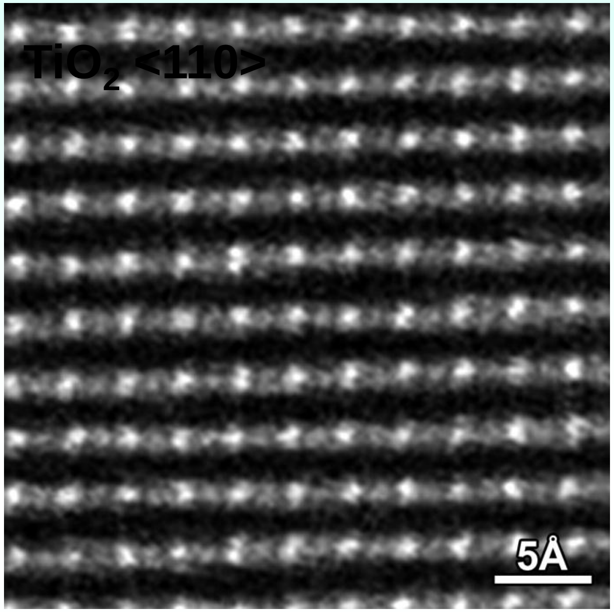


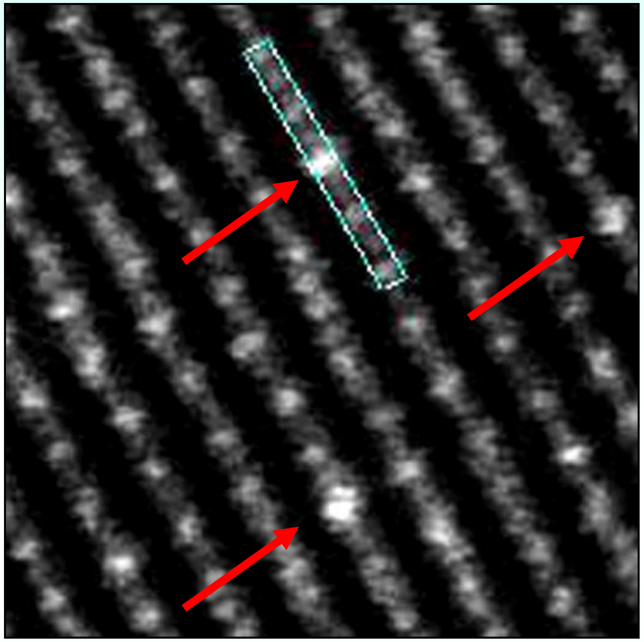


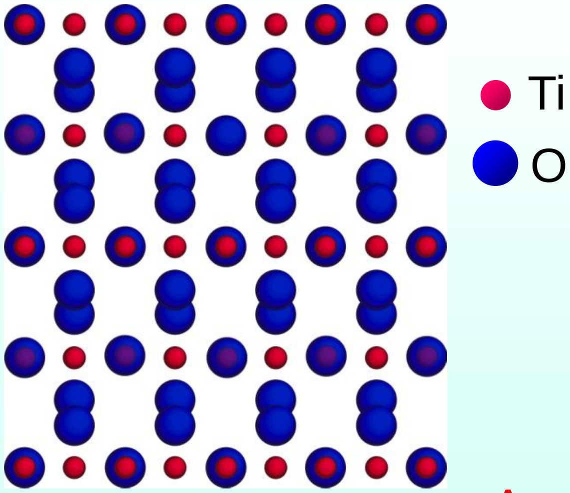
Heavy Au particles can be clearly imaged by Z-contrast STEM !

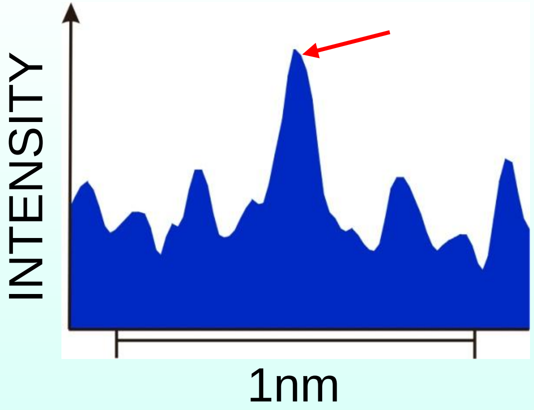
Au single atoms on TiO_2 (110) surface

Au attached on Ti-O columns







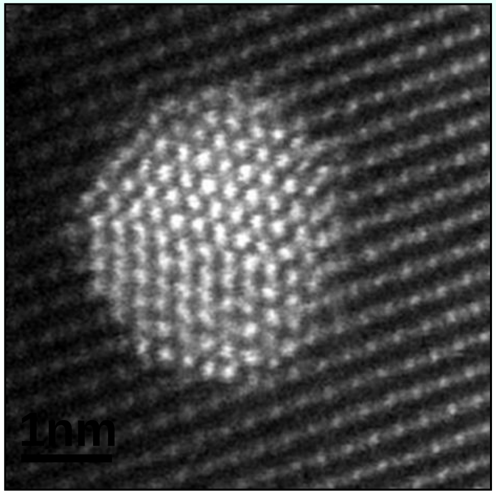


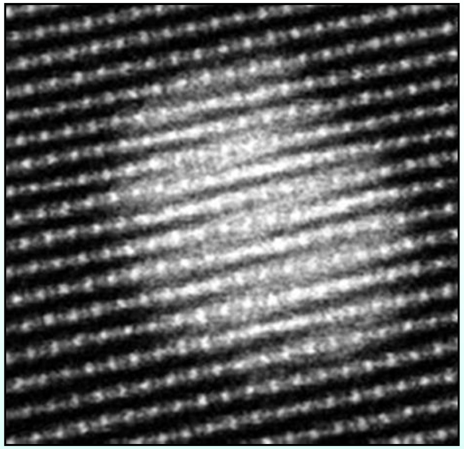
Au single atoms attached to the specific surface sites

Au-TiO_2 crystal orientation and interface structures

PRL(2007)

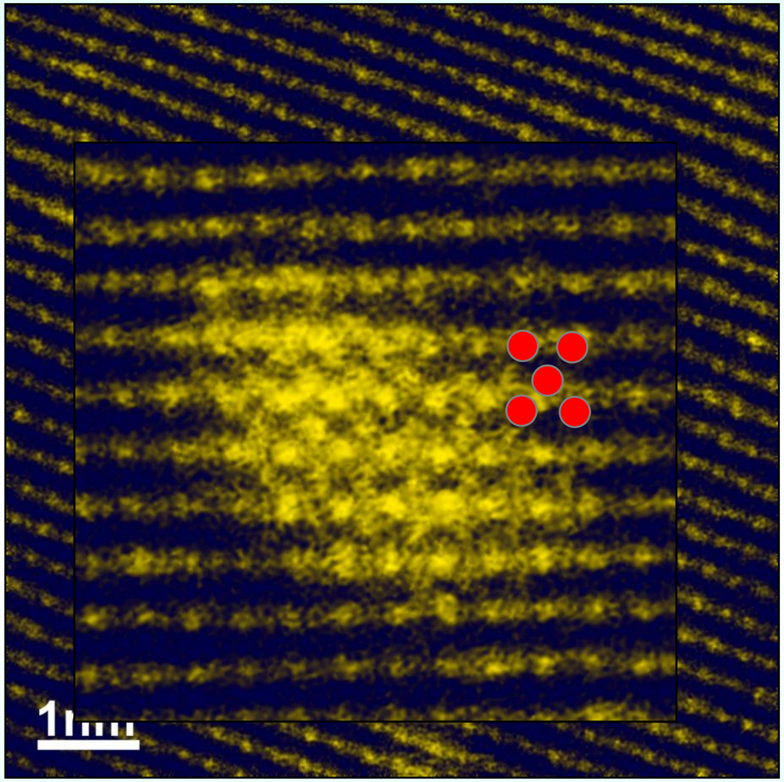
Au size >3nm





Au and TiO_2 have no lattice coherency

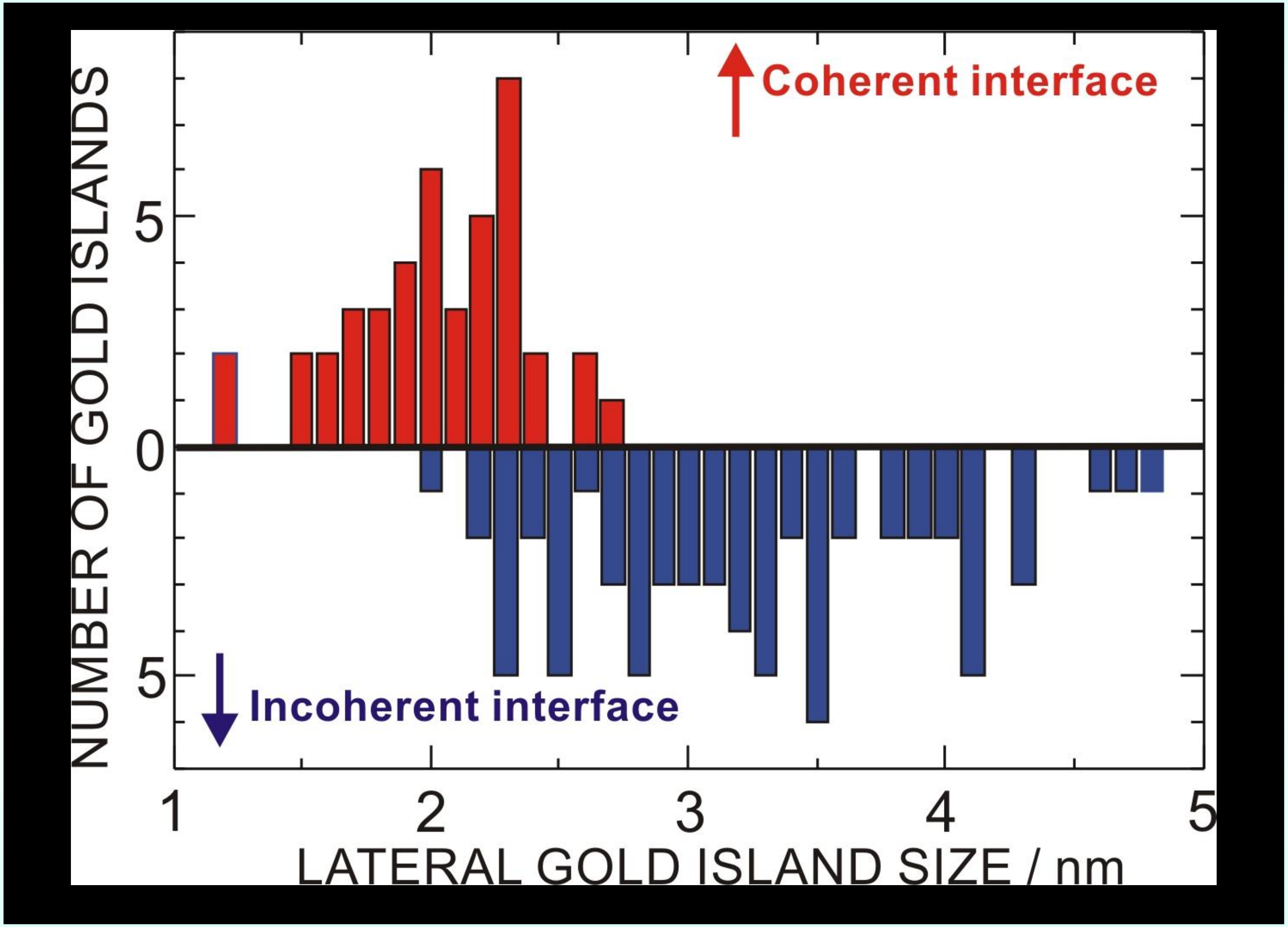
Au size <3nm



Unique epitaxial Au structure on TiO_2 surface

Nano-coherent interface between Au and TiO_2

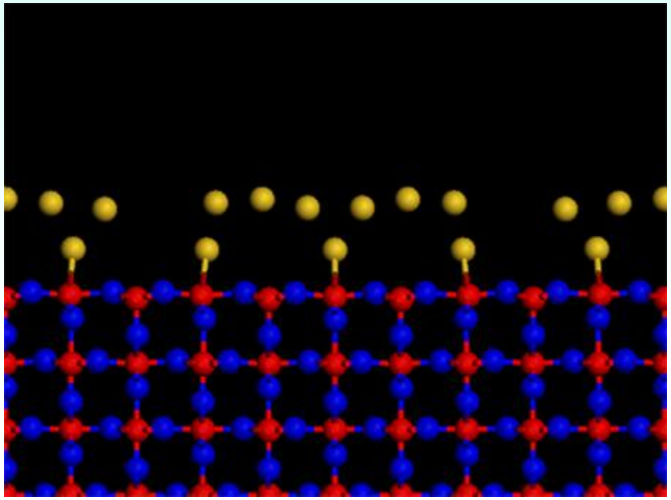
Size dependent “coherent↔incoherent” interface transition

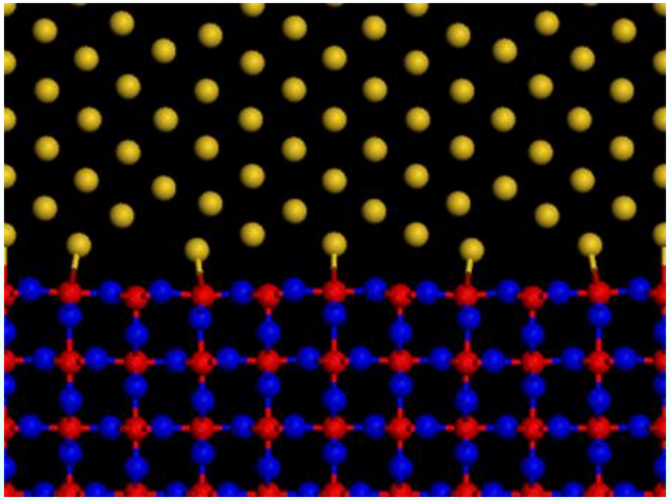


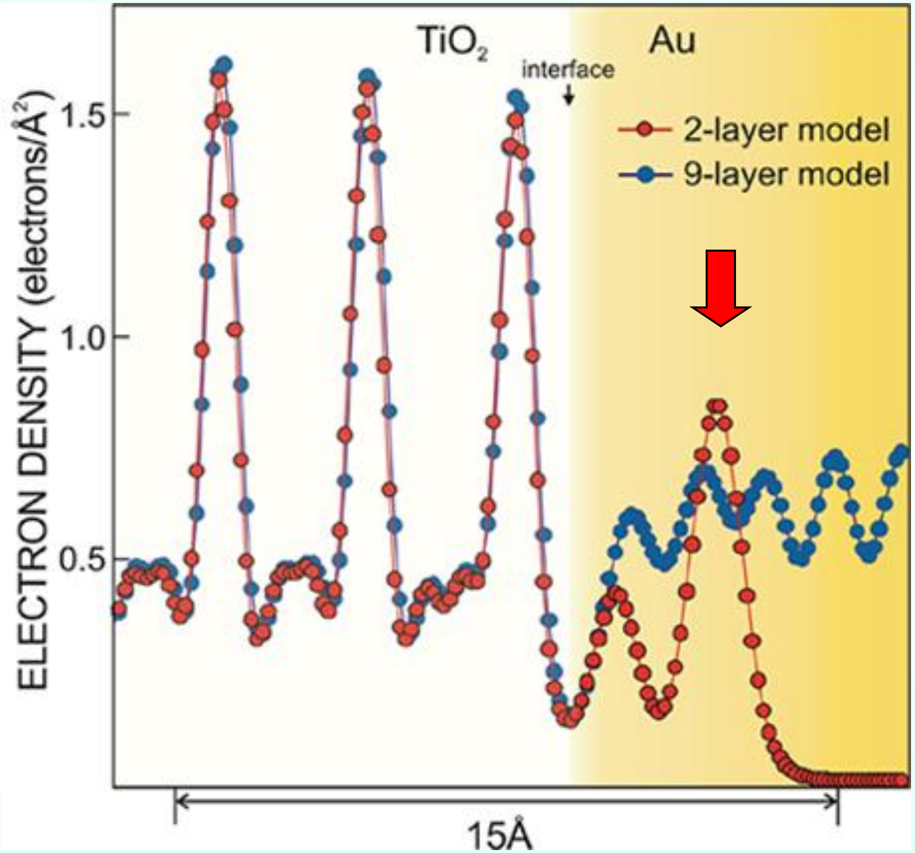
Au-TiO_2 interface structures dramatically change according to the Au sizes!

PRL(2007)

Electronic structures of Au nanoislands on TiO_2







When Au nanoislands are very small, TiO_2 substrate drastically changes their atomic as well as electronic structures through unique interface structures!

Short Break !

Gallery (Another Example (HAADF-STEM))

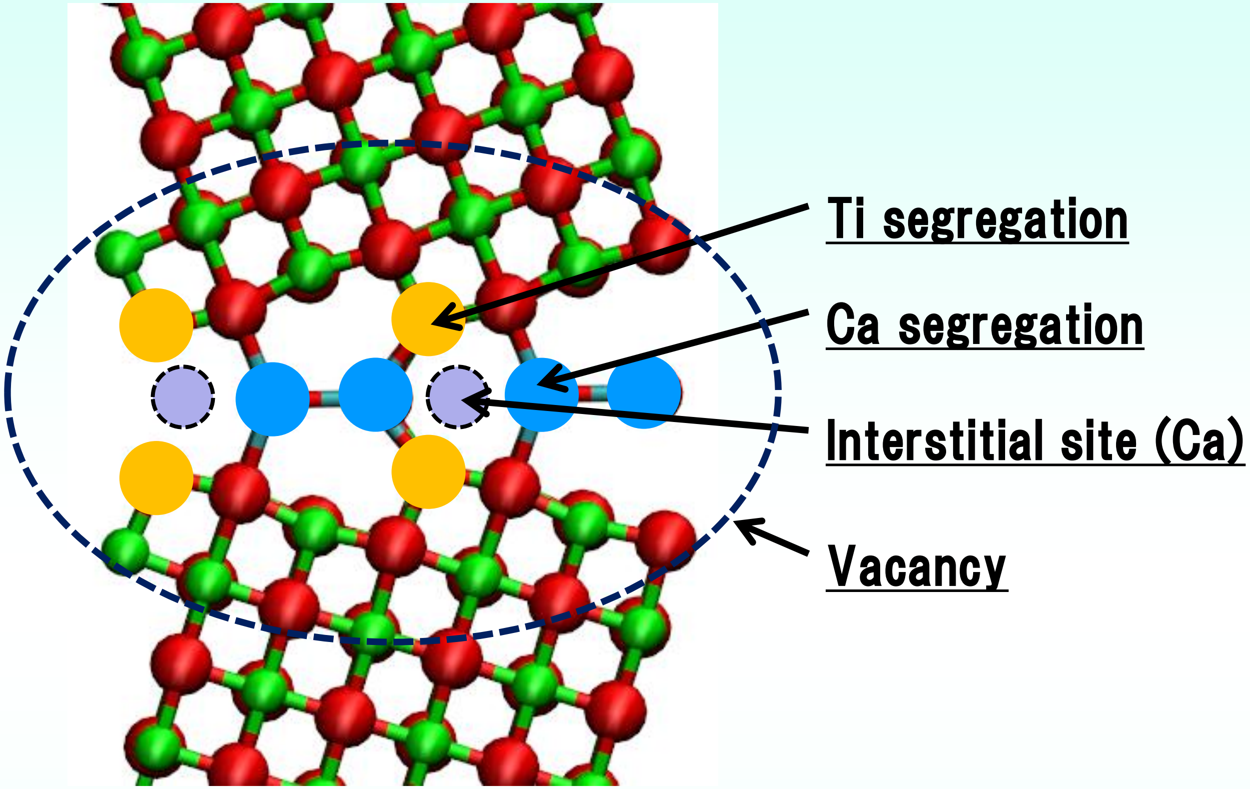
How STEM is powerful to reveal the nature of materials!

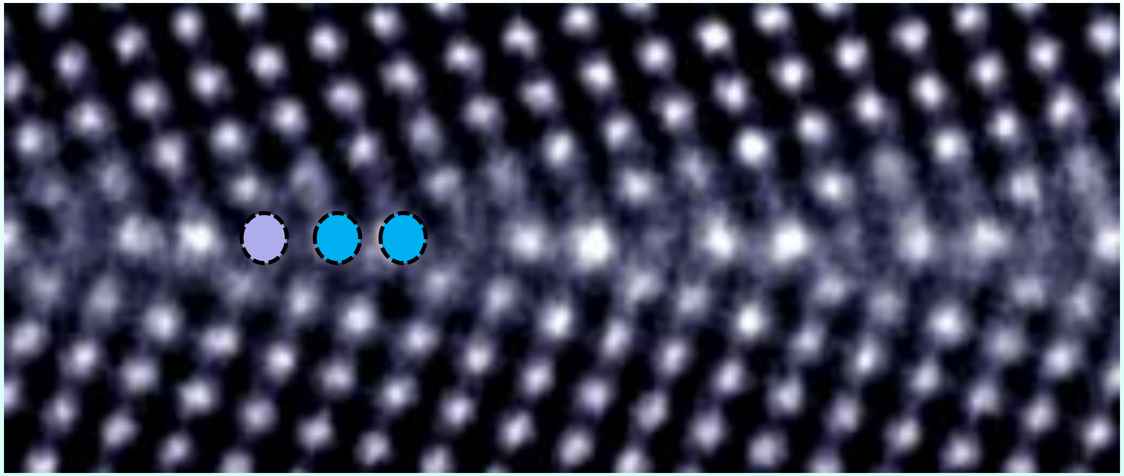
$Ca^{2+}Ti^{4+}$doped MgO

Ce doped c-BN

Eu doped Al_2O_3 (Dislocation)

Ca^{2+}+Ti^{3+} co-doped GB (MgO Σ5GB)



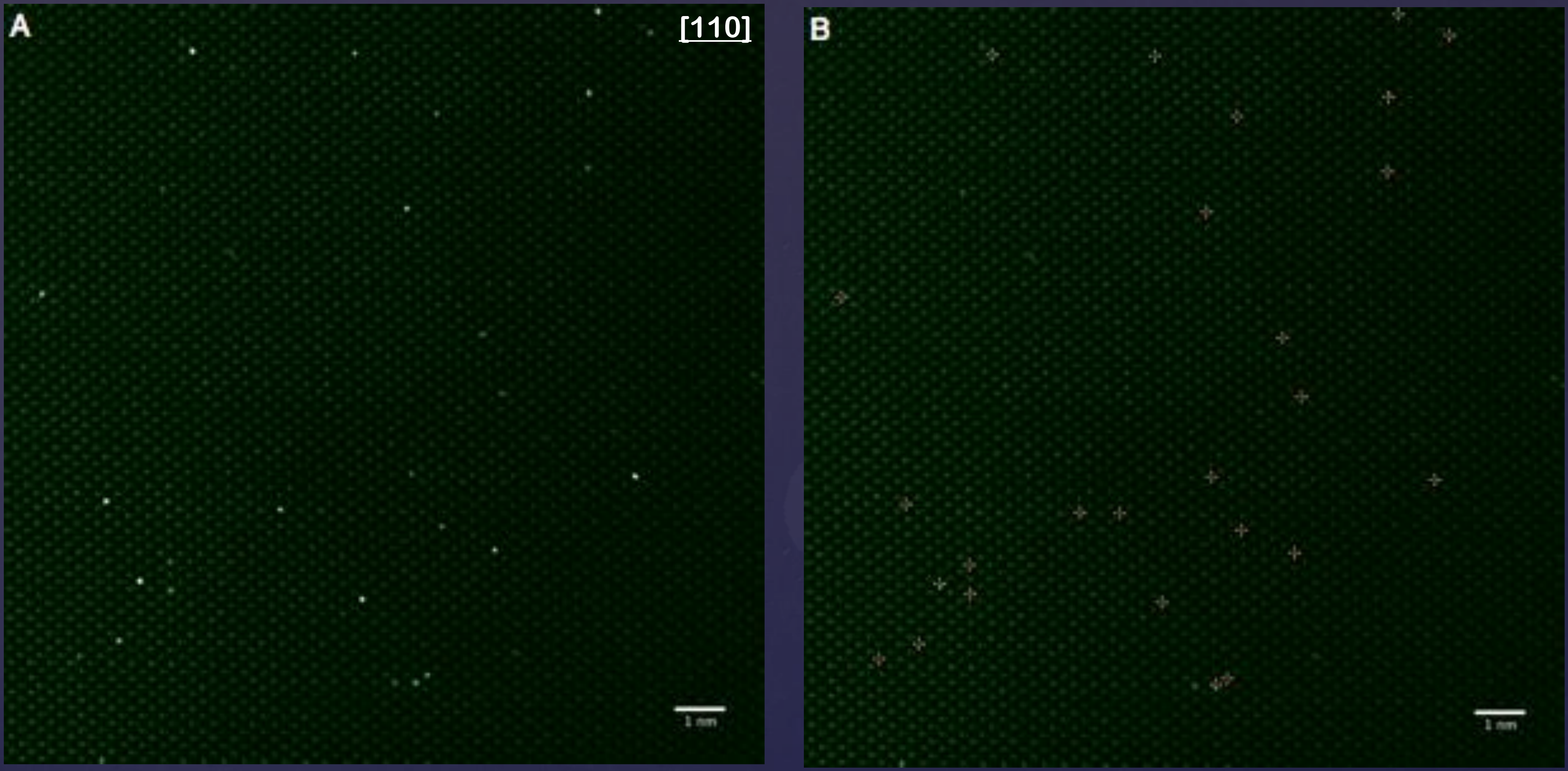


GB Ordered Segregation Superstructures

Nature (2011)

Single Atom Imaging in a crystal

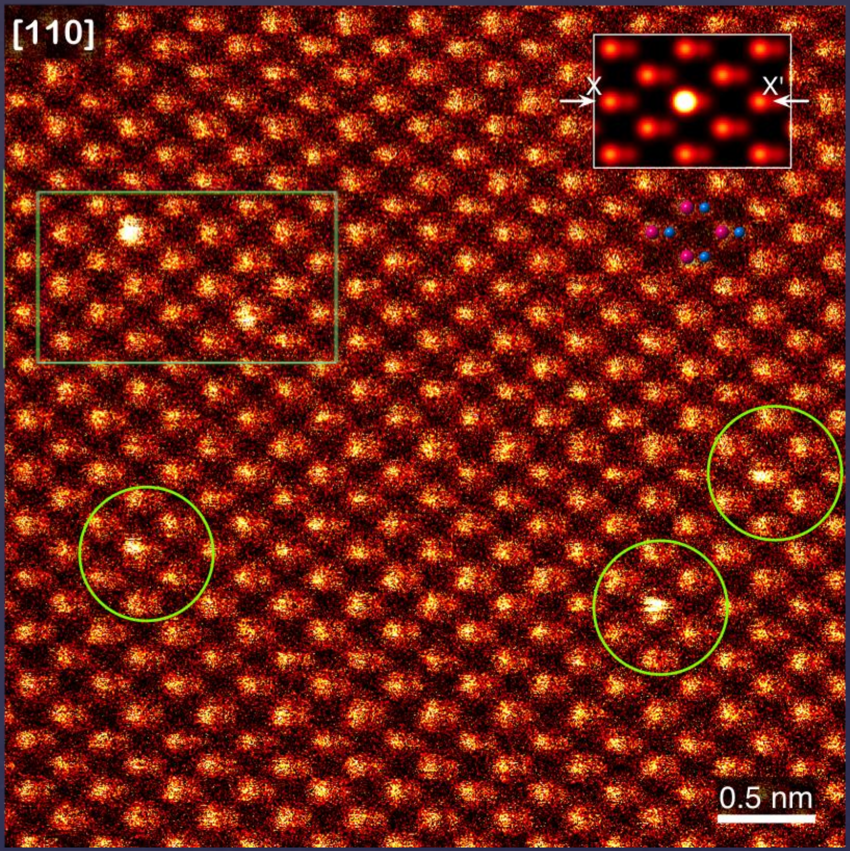
Spatial distribution of Ce atoms in c-BN (Solid Solution)

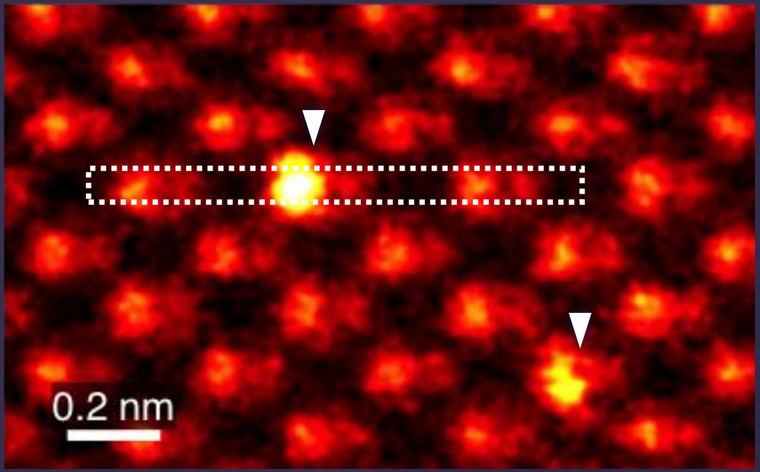


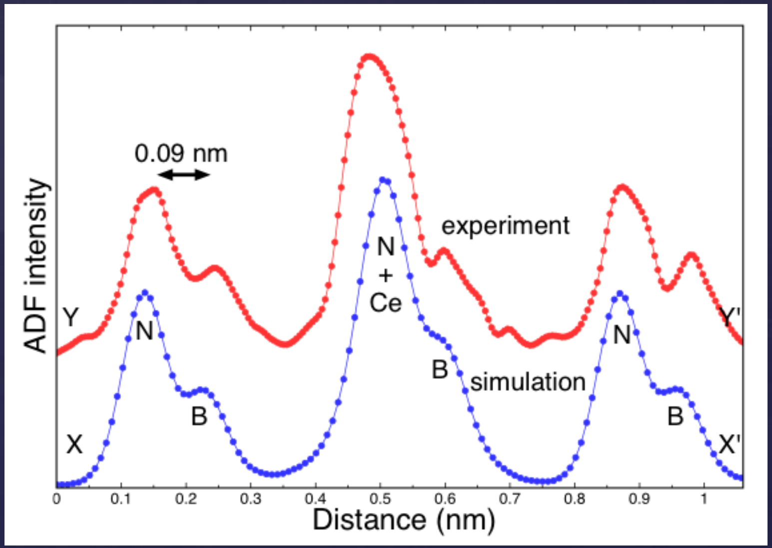
ZB = 5, ZN = 7, ZCe = 58

- Ce distribute as “isolated” single atoms
- brightness: depth or overlap
- thickness measurement: EELS
- atom counting by local maxima
- < 20 nm, ignoring overlap

Atomic site of single Ce atoms in ADF STEM







~8 pA, 200 kV BN-dumbbell: ~0.9 Å

Ce occupies N-antisite (cation-anion substitution) PRL(2013)

Short Break

Great Breakthrough in Materials Science!

$Ca^{2+}Ti^{4+}$ doped MgO
Complicated GB segregation

Ce doped c-BN
Solid solution

Eu doped Al_2O_3 (Dislocation)
Cottrel atomosphere

STEM-Theoretical Calculation-Materials Design

(1)Segregated Dopants at Ceramic Grain Boundaries

- Single dopant (Al_2O_3 : Y^{3+})
- Co-dopant (Al_2O_3 : Ca^{2+}+Si^{4+})
- Functional materials (ZnO: Pr)

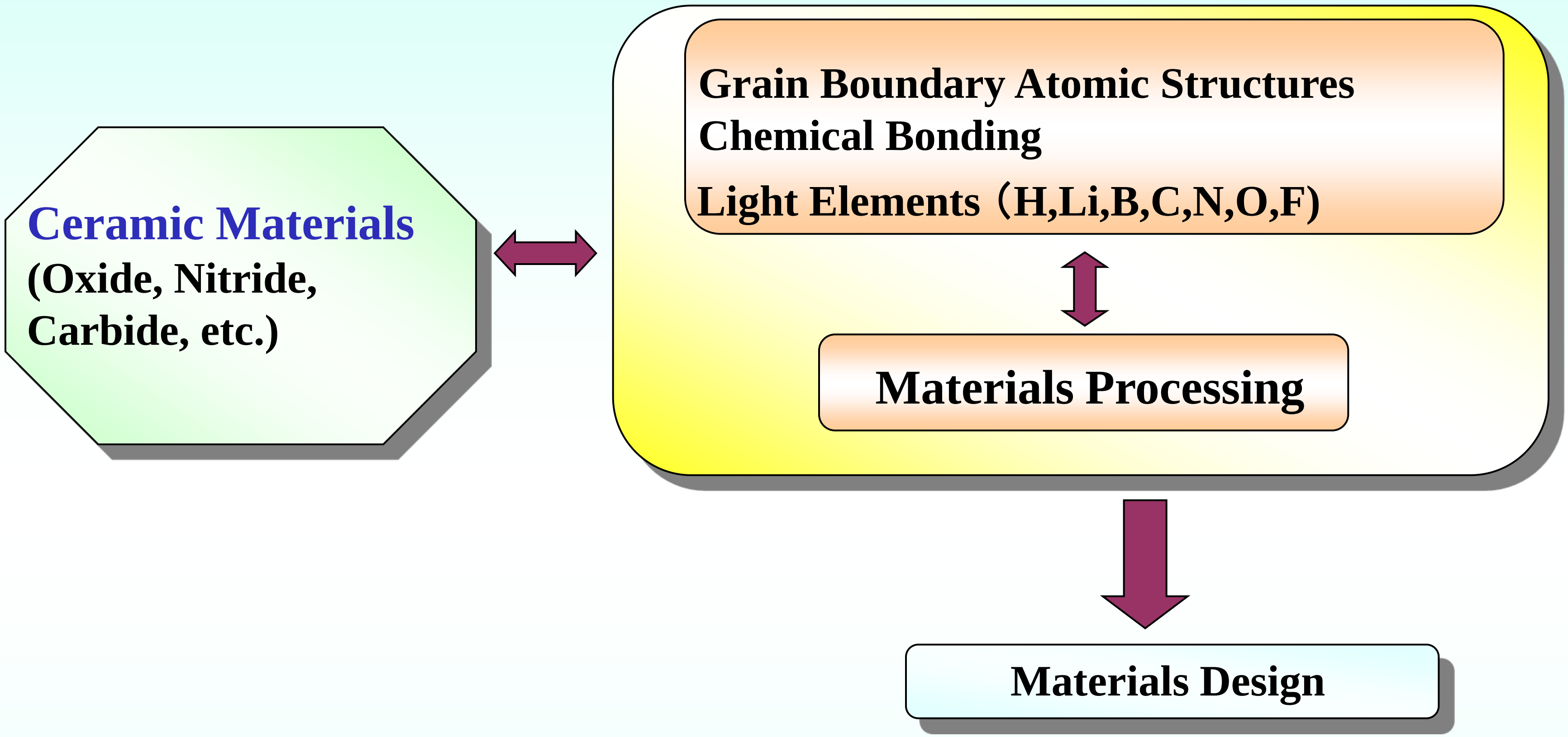
(2)Catalyst (Au-nanoparticle on TiO_2)

(3) STEM Annular Bright Field Imaging

Direct Observation of Li Ions and H

($LiMn_2O_4$, $LiCoO_2$,VH_2)

Background



New Approach

- **Visualization of Light Elements (Direct Observation)**

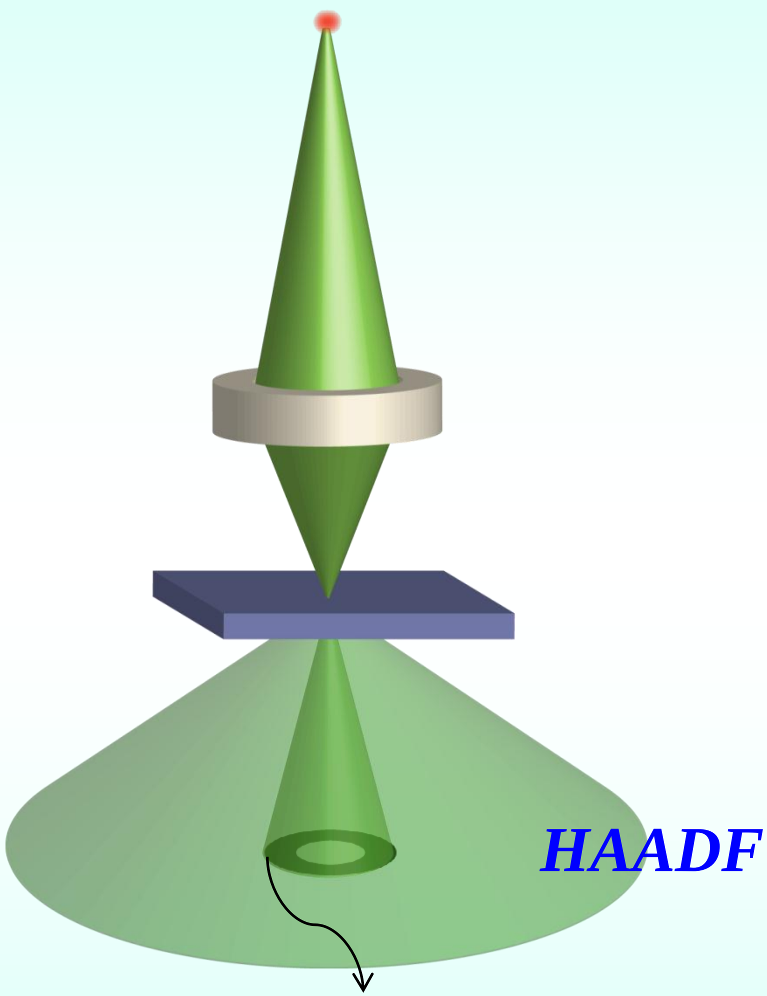
STEM: Annular Bright Field (ABF)

Univ.Tokyo, JFCC, JEOL

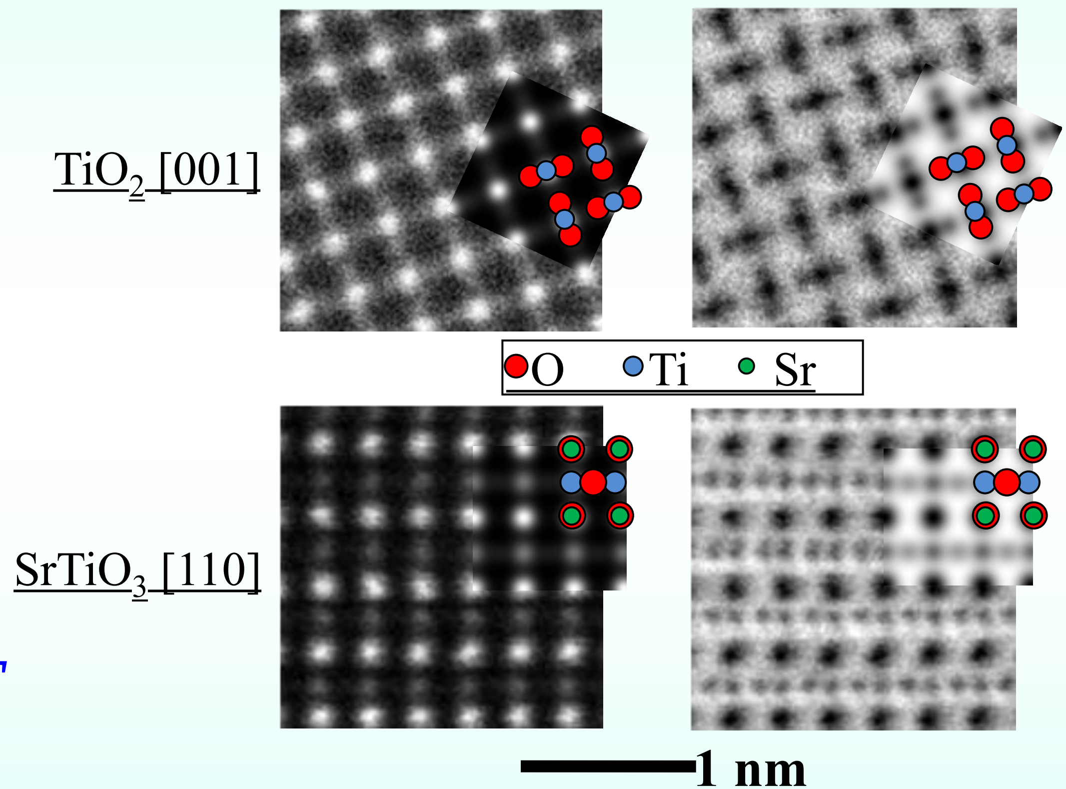
Findlay et al, APL (2009)

Okunishi et al, M&M (2009)

JEM ARM-200F, 200 keV, α = 22 mrad
HAADF: 90–170 mrad, BF: 11–22 mrad

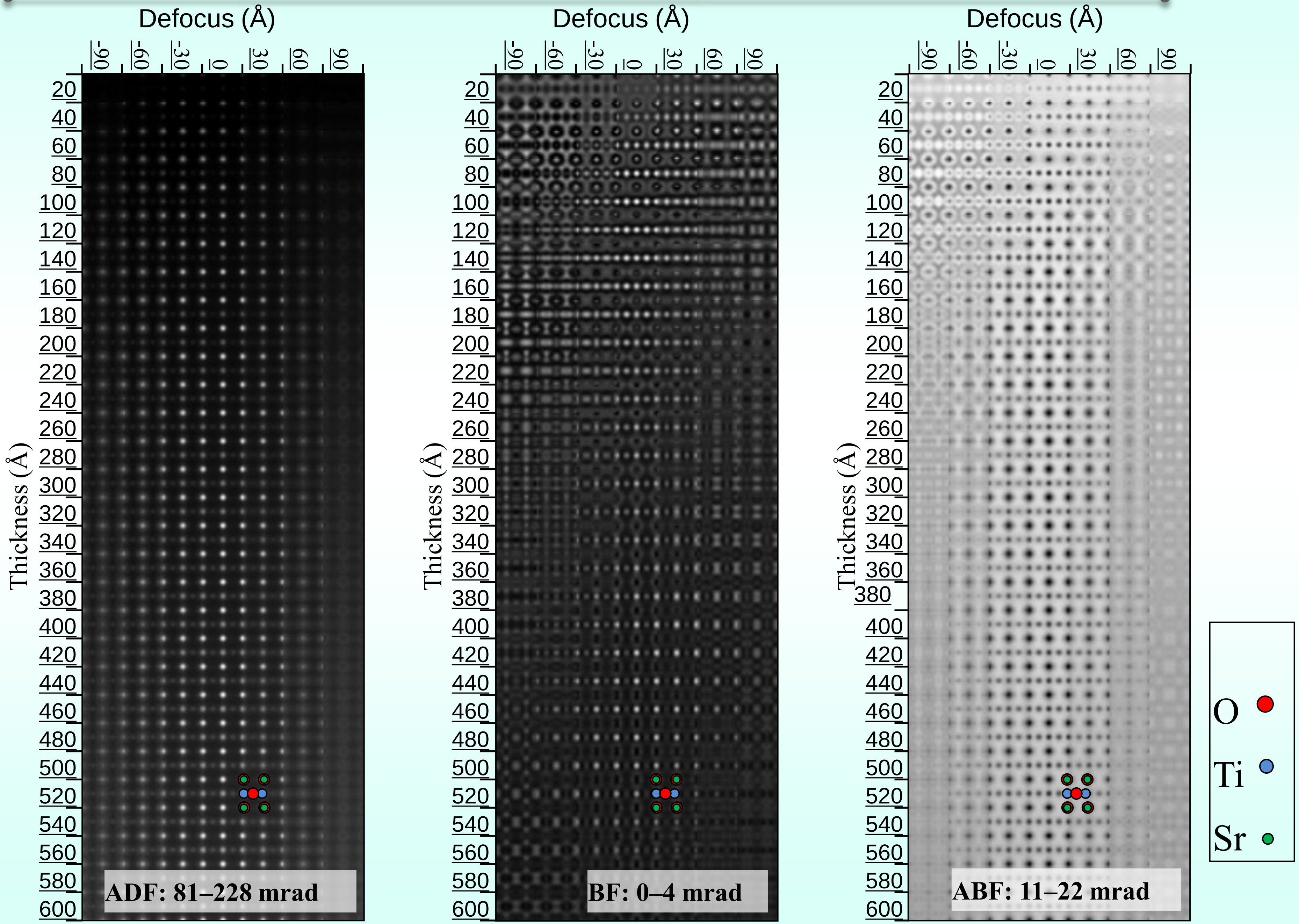


Annular bright field (ABF) detector



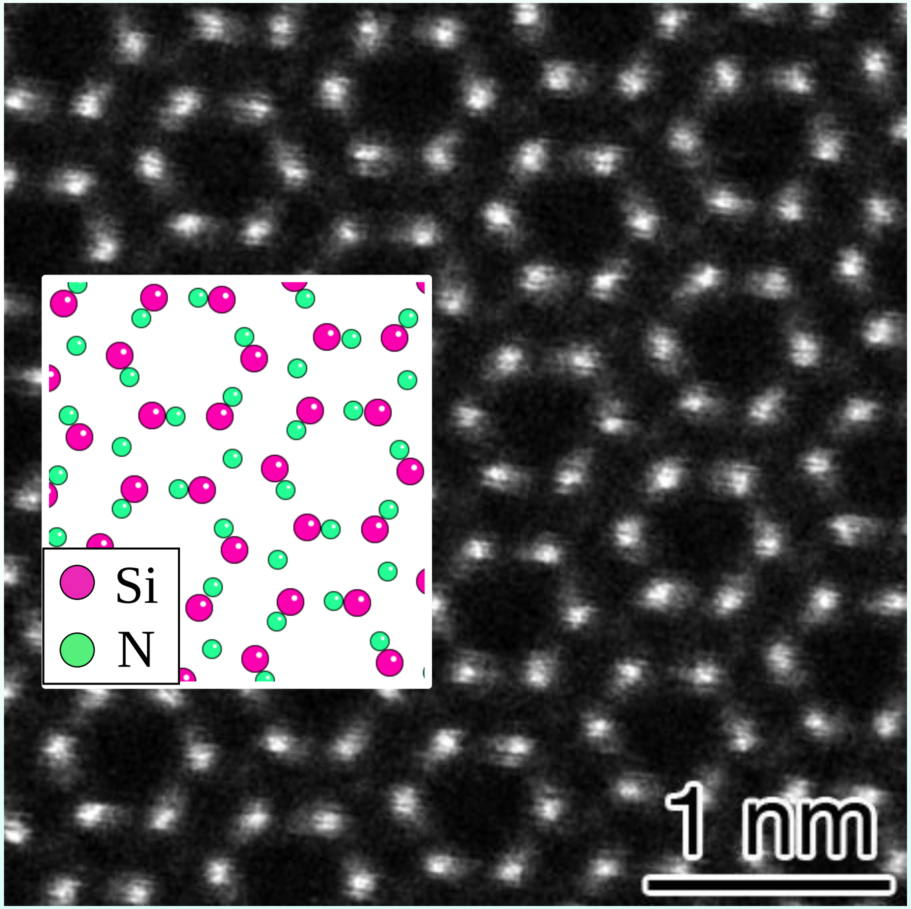
- ABF imaging shows light and heavy columns simultaneously.
- Seems to be robust over wide thickness range.

Defocus-thickness map simulations: $SrTiO_3$ [011]

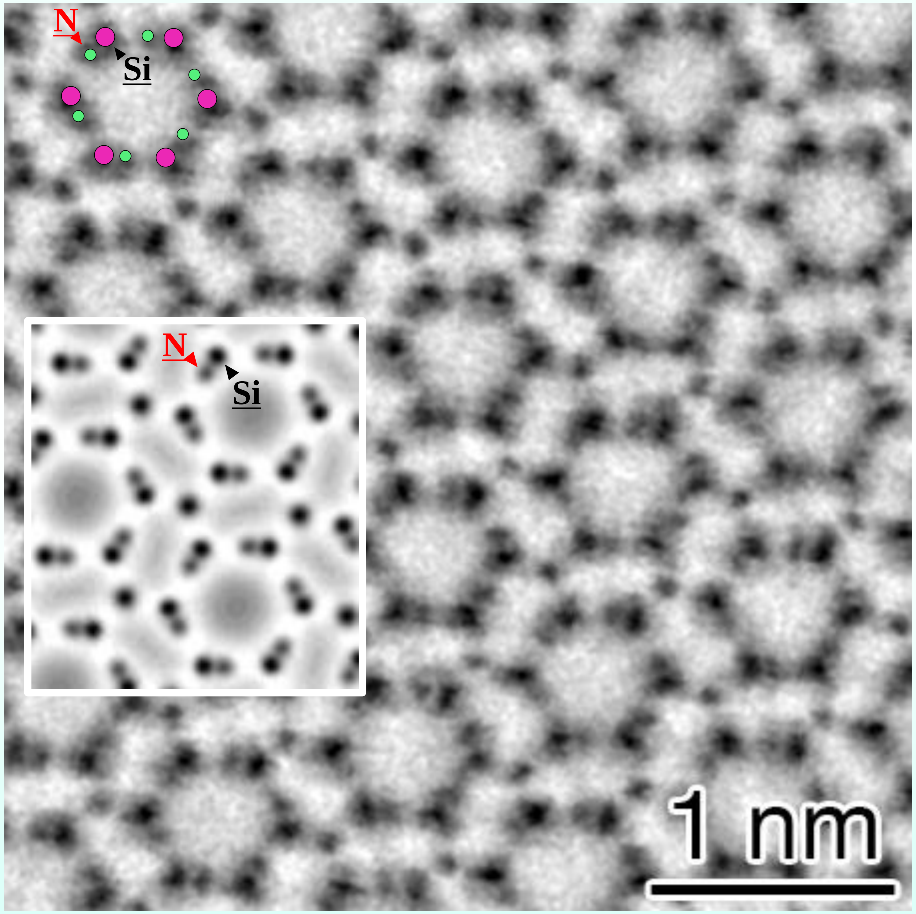


STEM images of β-Si_3N_4 [0001]

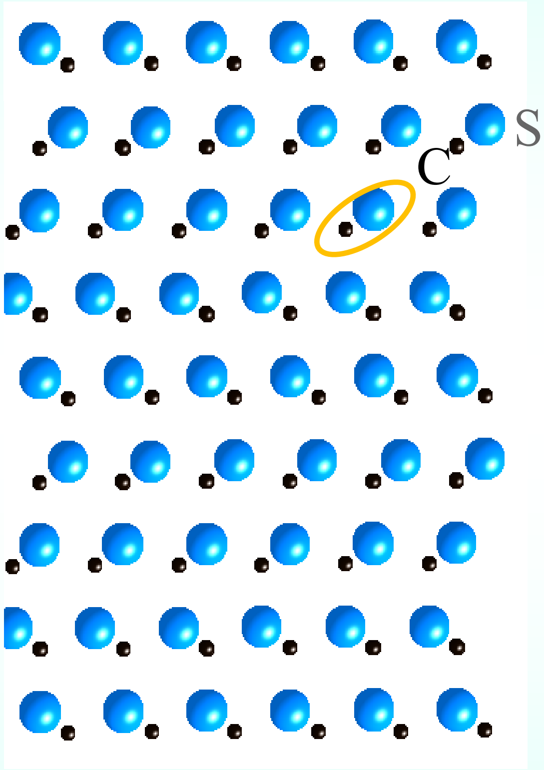
HAADF



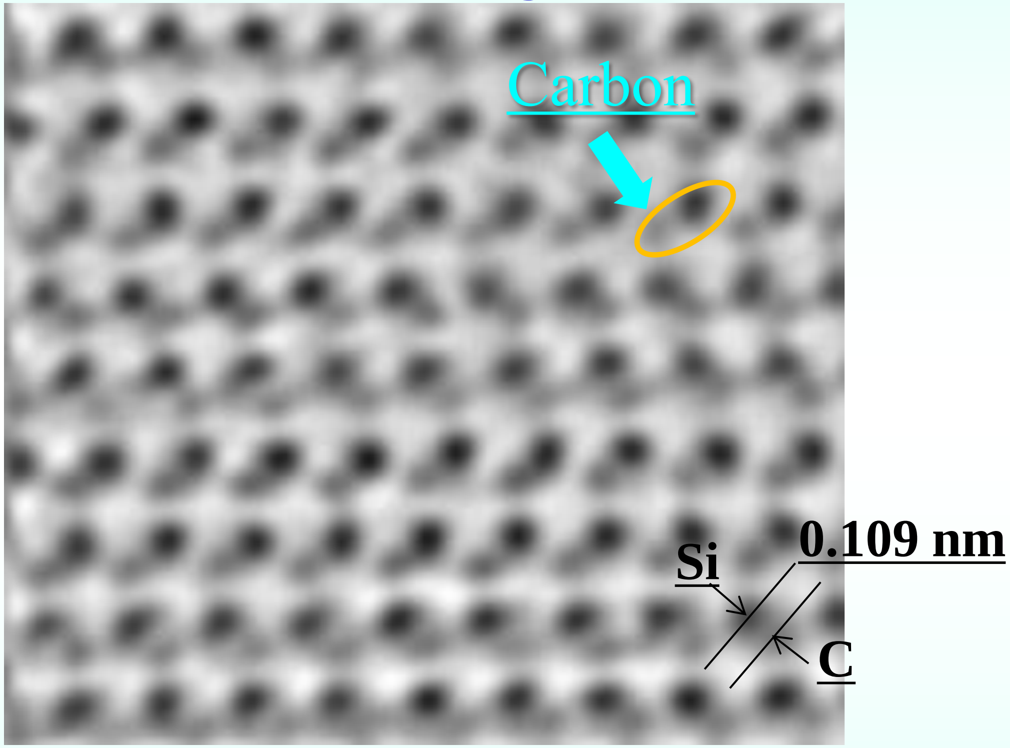
ABF



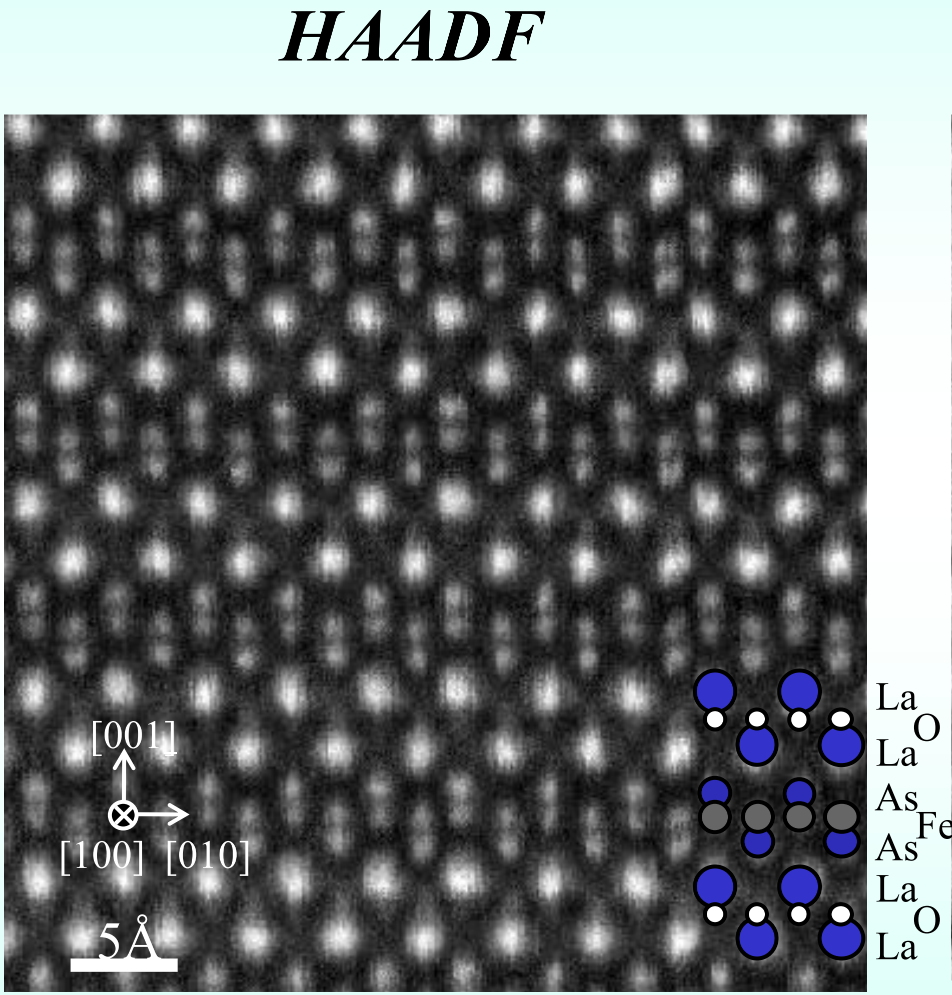
4H-SiC [11$\bar{2}$0] projection

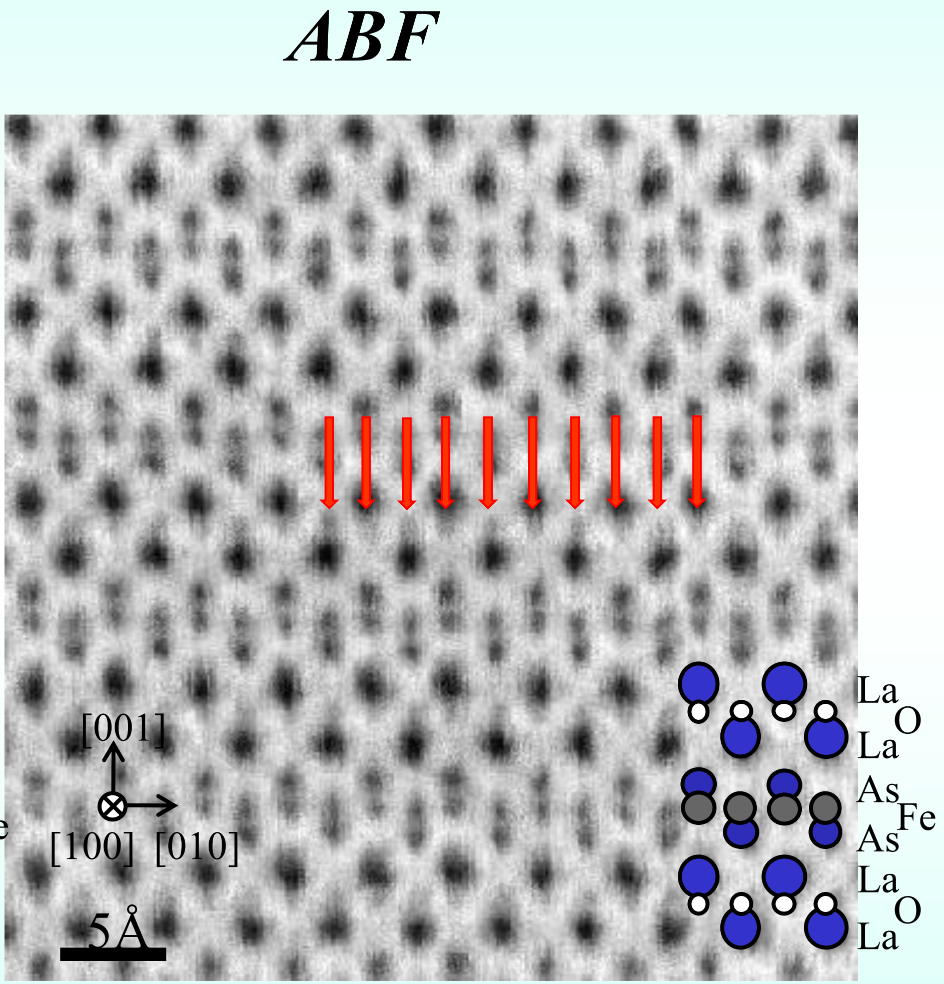


ABF STEM image



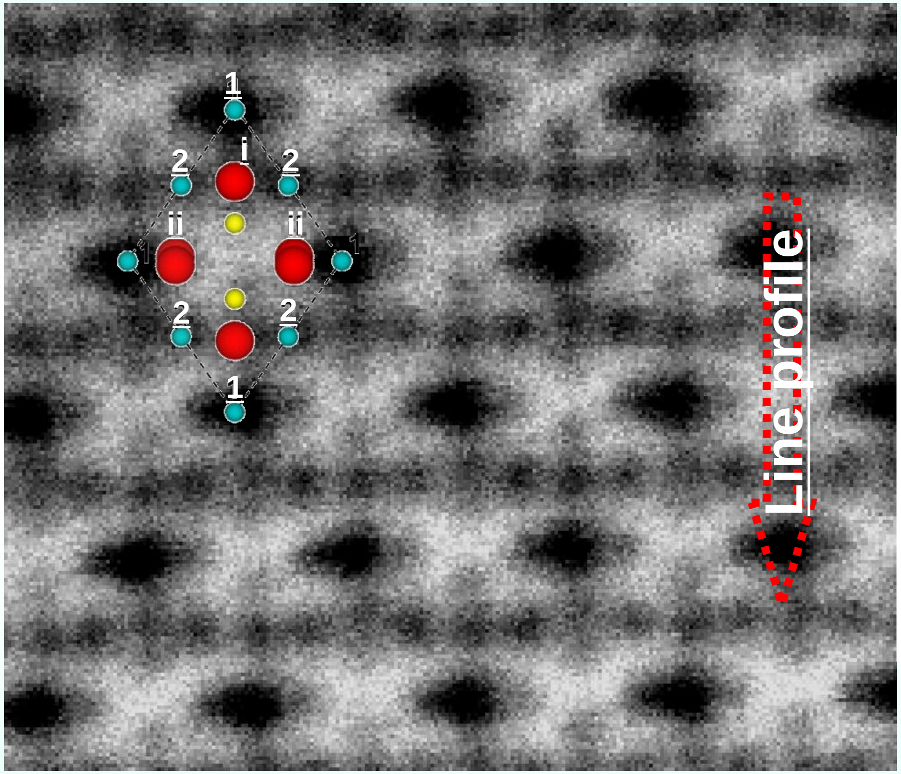
STEM Images of $LaFeAsO_x$



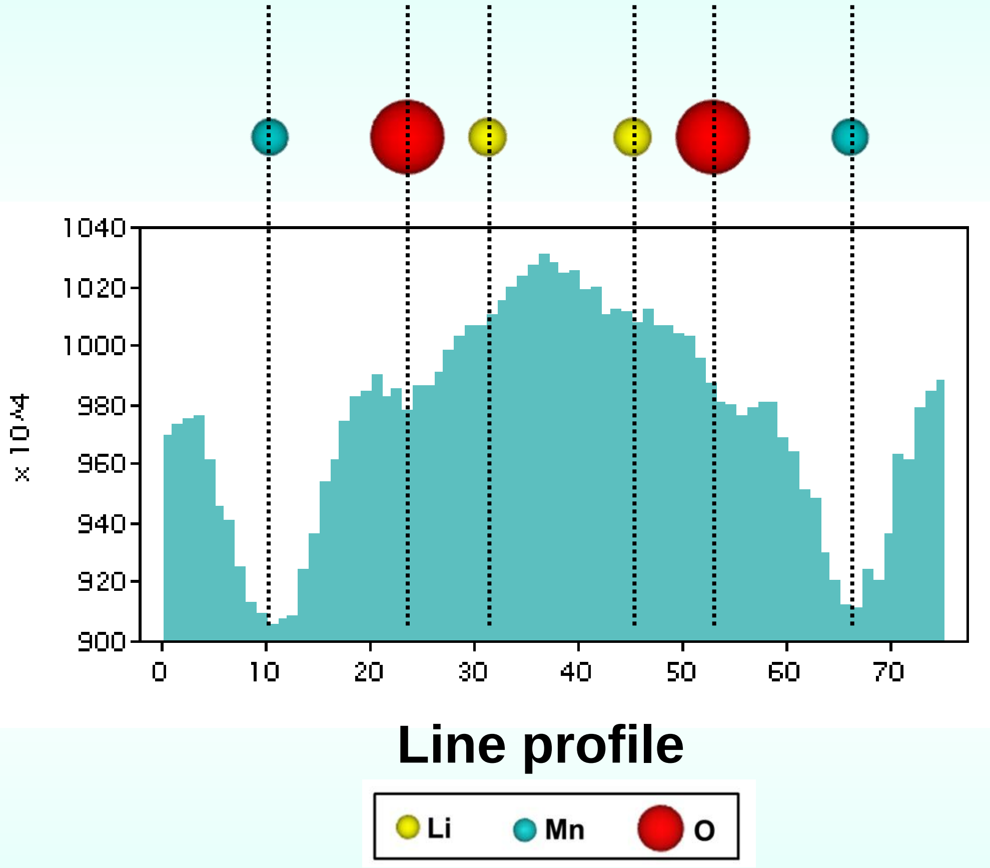


Direct observation of Li in $LiMn_2O_4$ spinel by ABF technique in STEM

ABF: α=25 mrad β= 8-25 mrad



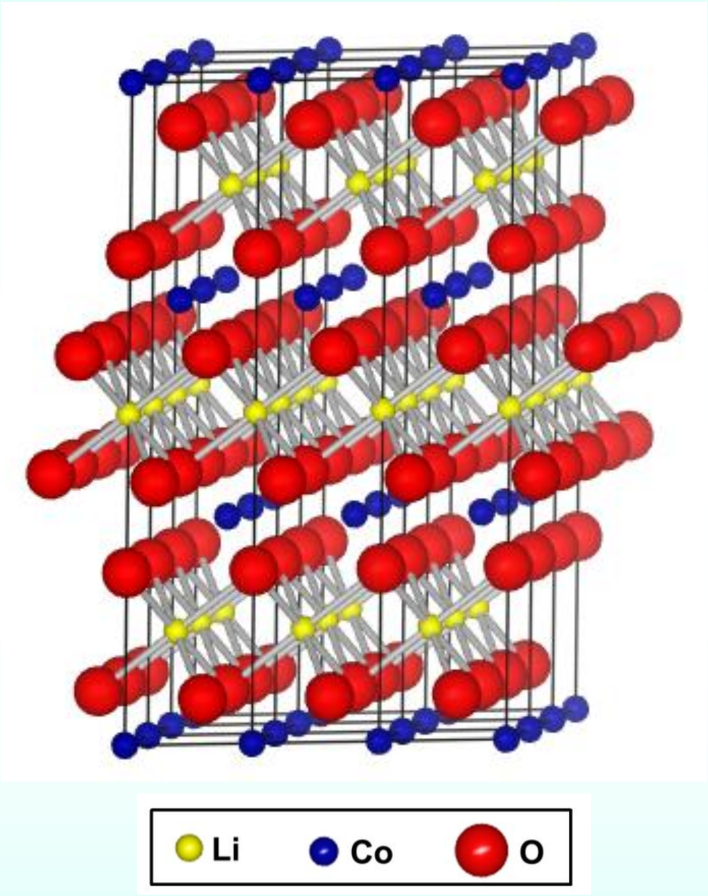
$[110]_{LiMn_2O_4}$



Angewandte Chemie (2011)

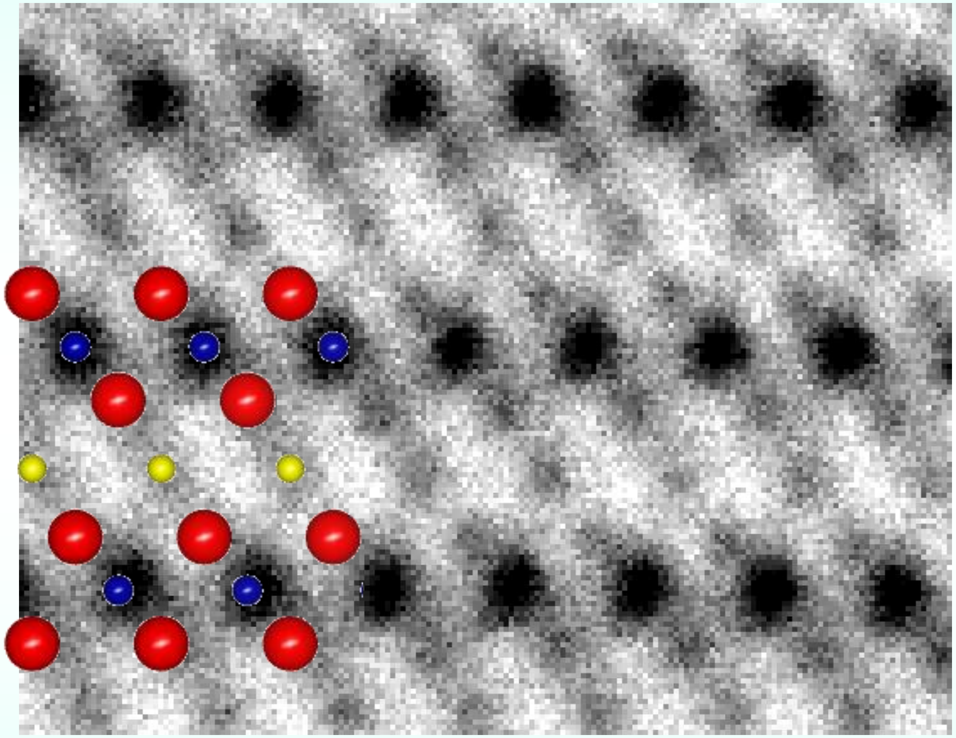
Direct observation of Li in $LiCoO_2$ by ABF technique in STEM

APL(2010)



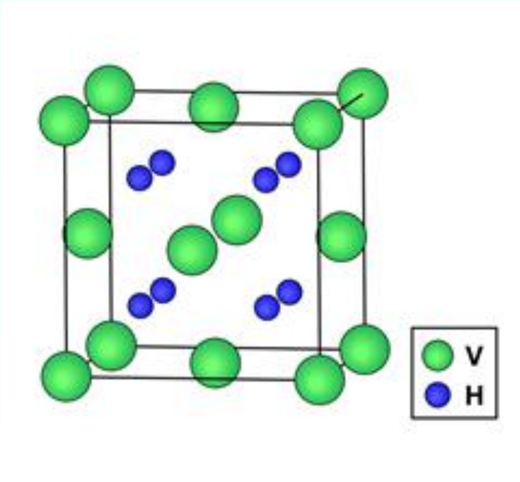
$LiCoO_2$:
S.G. : R-3m (166)
a = b = 2.84 Å, c = 13.95 Å

ABF: α=25 mrad β= 8-25 mrad



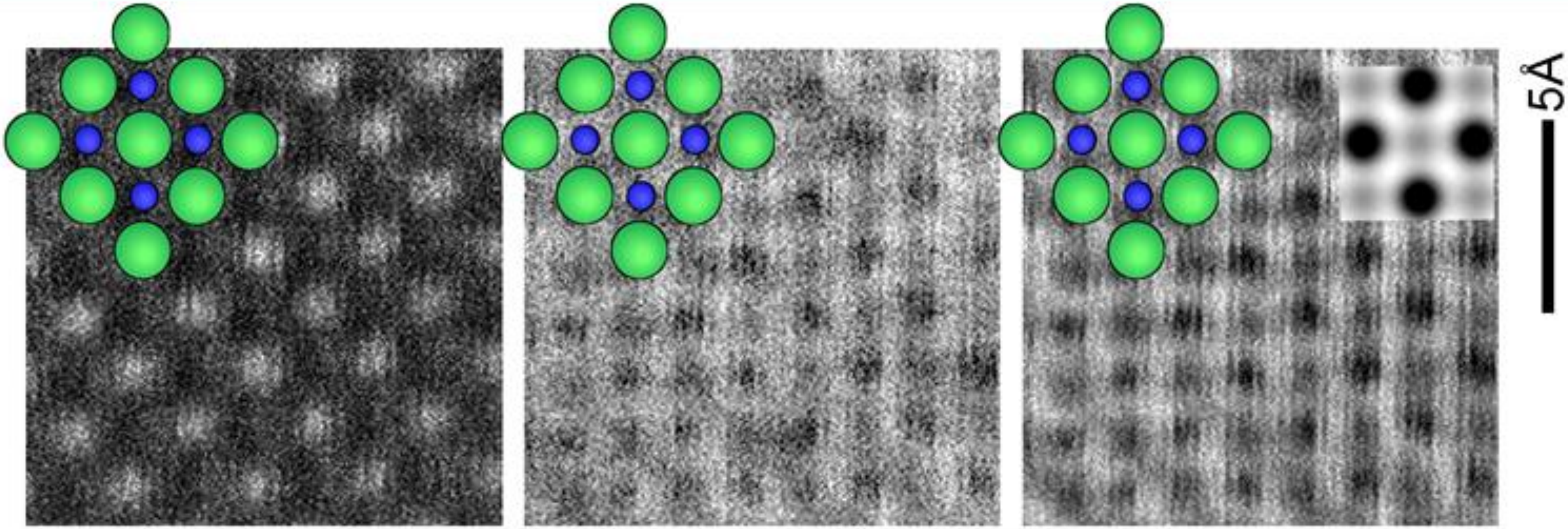
$[11\bar{2}0]_{LiCoO_2}$

Li can be clearly seen in this image



VH_2

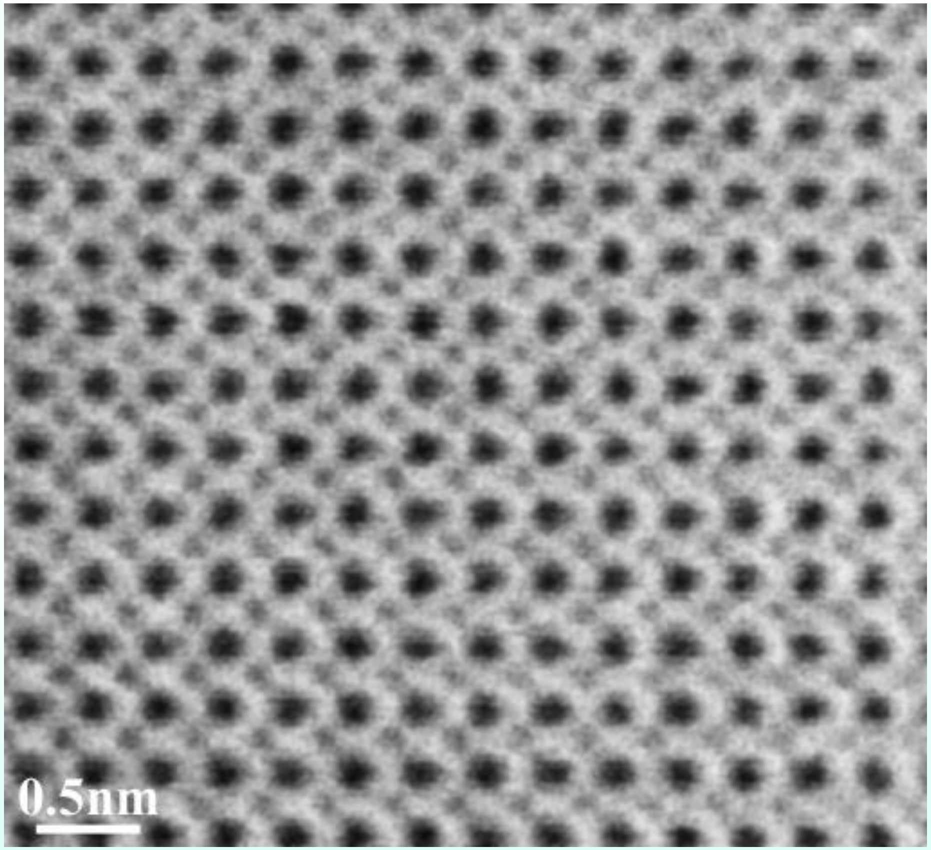
APEX(2010)

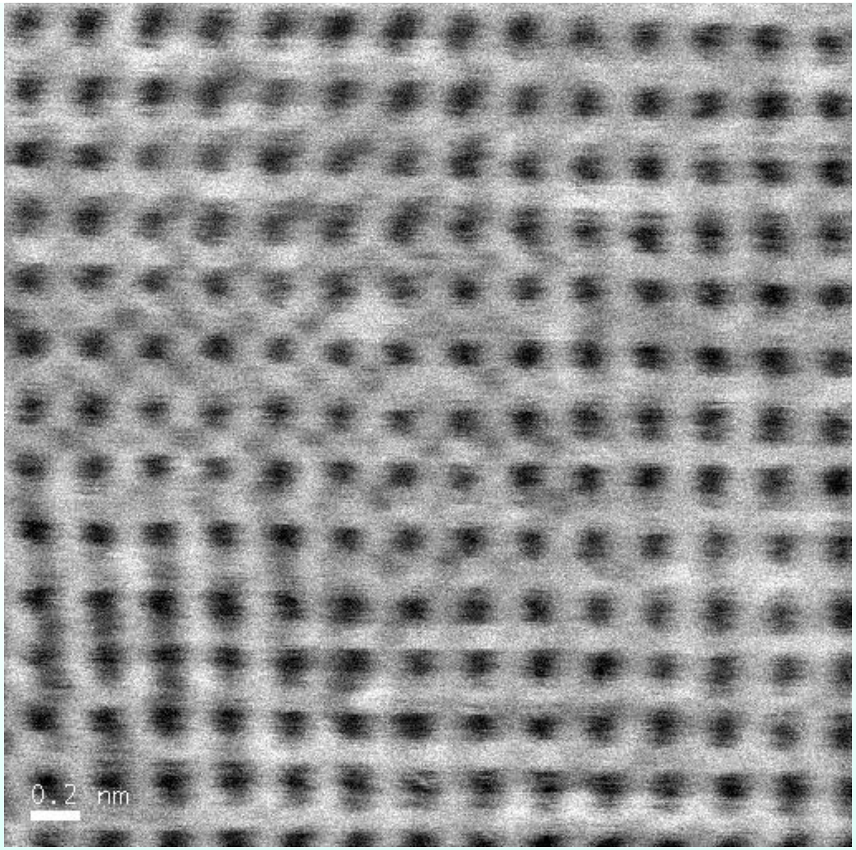


HAADF **ABF** **Filtered Image**

ABF-STEM Images

(α = 25 mrad, β = 8–26 mrad)





High Resolution STEM +Quantitative Analysis

- **Cs-corrected STEM (<1 Å)**
- **Theoretical Calculation (First Principles, Lattice Static, MO etc.)**

·Segregated Dopants at Ceramic Grain Boundaries,

Three Dimensional Observations, Single atom imaging (Al_2O_3 : Y^{3+})

Super structure, Charge neutrality (Al_2O_3 : Ca^{2+}+Si^{4+})

Site of locally largest inter-atomic distance (ZnO:Pr)

·Catalyst (Au-nanoparticle on TiO_2), TiO_2 Surface

Small particles- Coherent interface

·STEM Annular Bright Field Imaging

Direct Observation of Li Ions and H ($LiMn_2O_4$, $LiCoO_2$,VH_2)

Thank you for your attention!

Univ.Tokyo

JFCC(Nagoya)

WPI,Tohoku Univ. (Sendai)

Thank you very much!