Role of Rare Metals in Material Technology
and the Way to Substitute them

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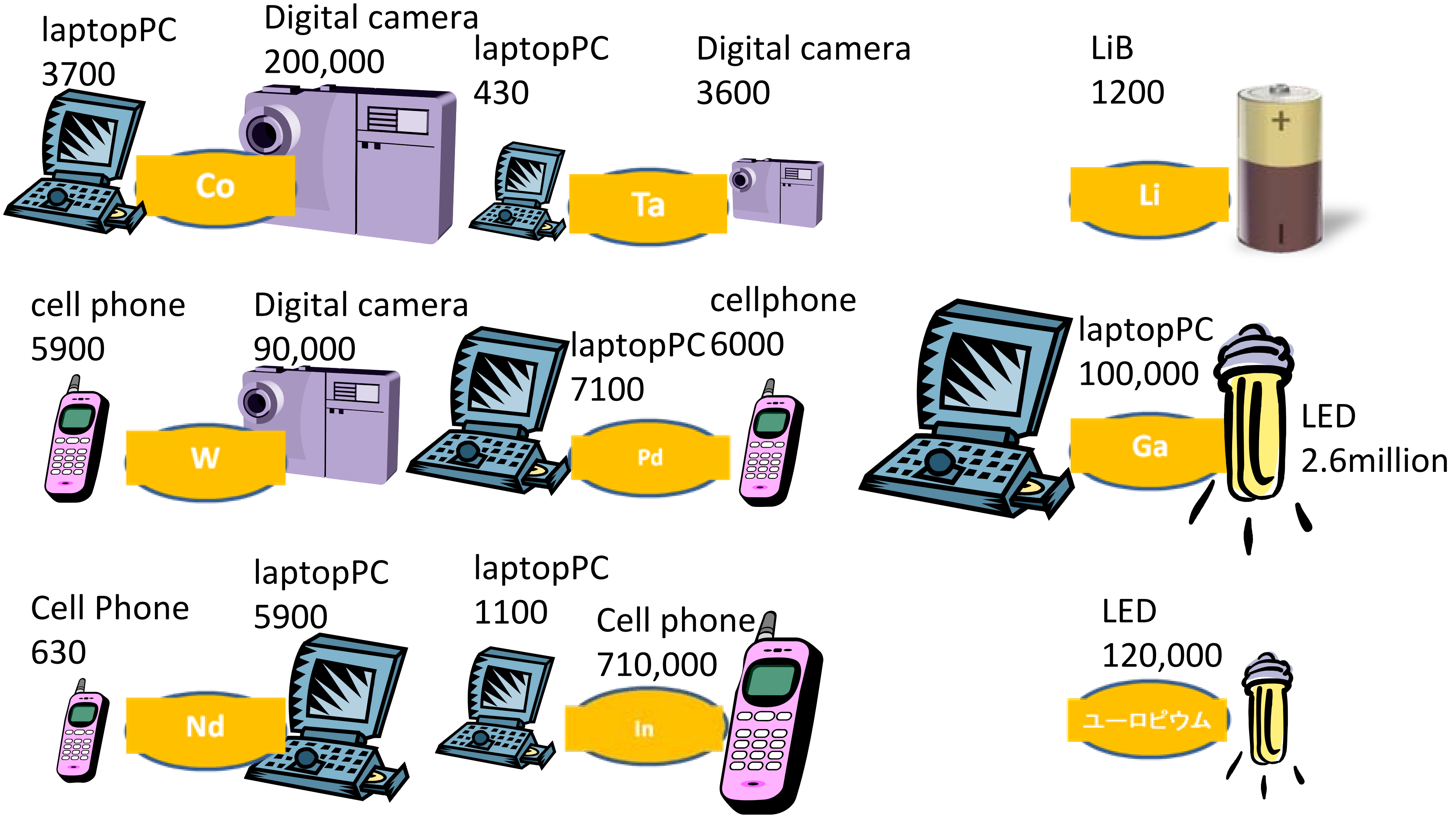
How many products are damaged by the lack of 1kg of rare metal



laptopPC
3700

Co

Digital camera
200,000

laptopPC
430

Ta

Digital camera
3600

Li

LiB
1200

cell phone
5900

W

Digital camera
90,000

laptopPC
7100

Pd

cellphone
6000

laptopPC
100,000

Ga

LED
2.6million

Cell Phone
630

Nd

laptopPC
5900

laptopPC
1100

In

Cell phone
710,000

ユーロピウム

LED
120,000

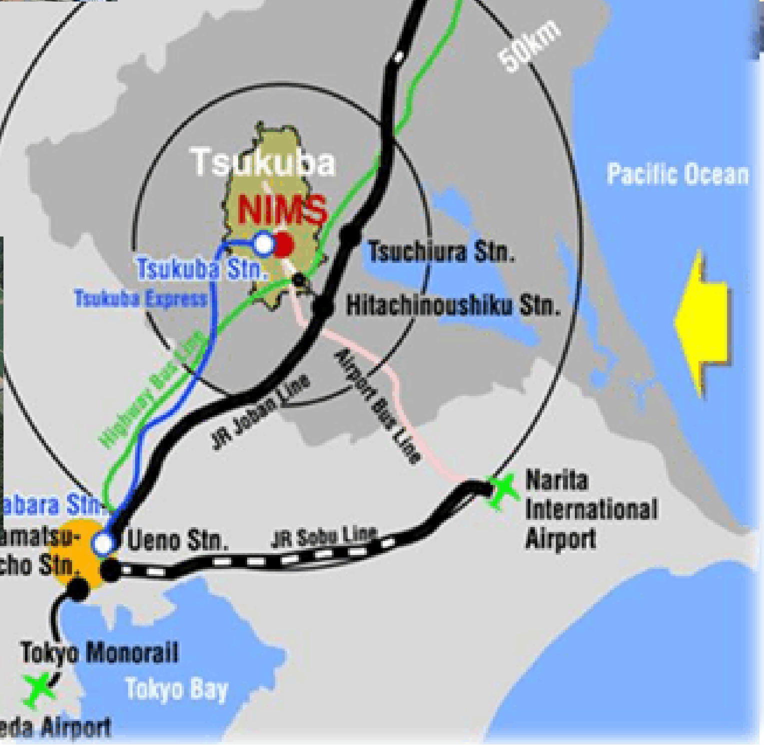
National Institute for Materials Science

under the control of MEXT

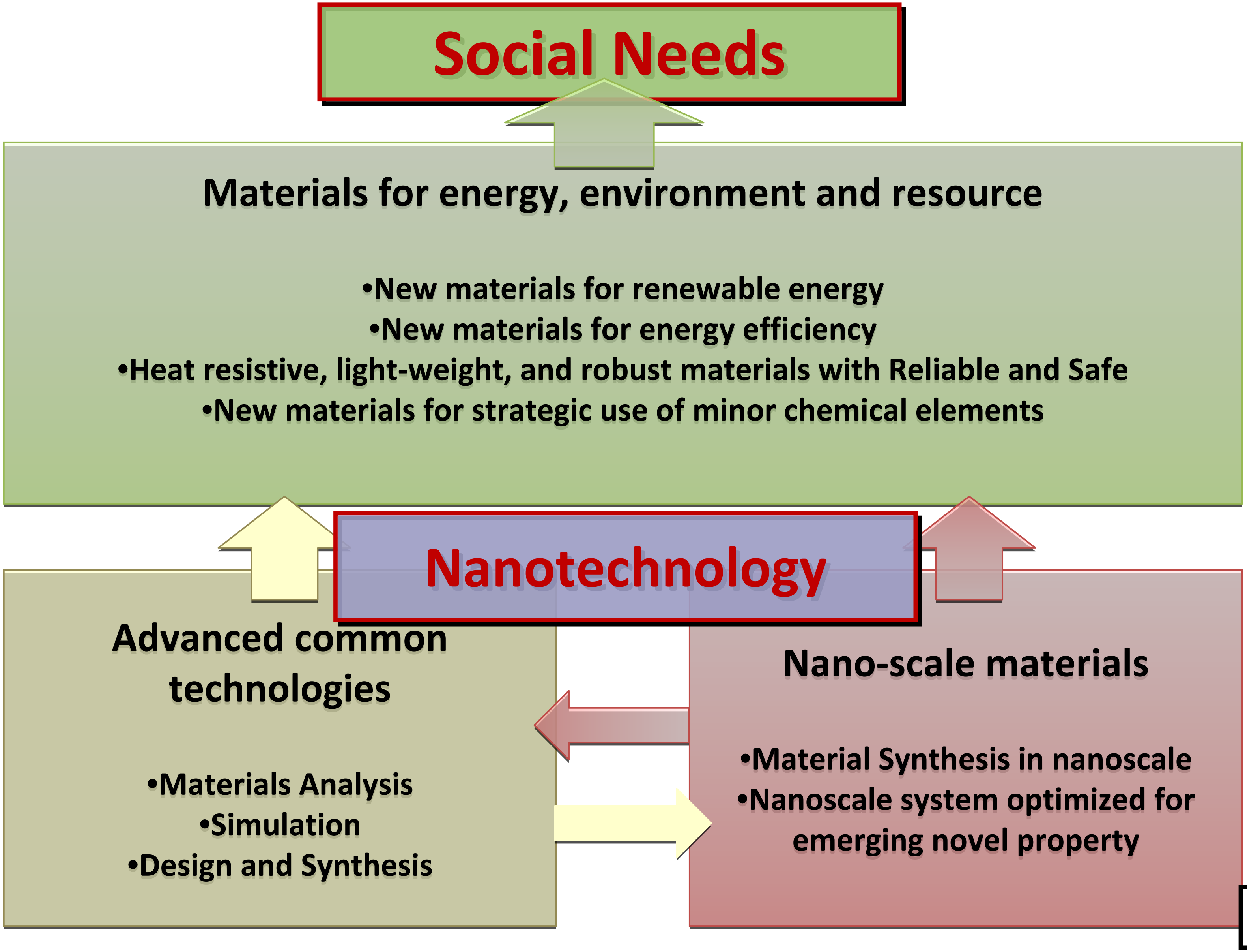
Sengen Site

Namiki Site

Sakura Site



Relationship among the three research field in the 3rd Five-year plan



Social Needs

Materials for energy, environment and resource

- New materials for renewable energy
- New materials for energy efficiency
- Heat resistive, light-weight, and robust materials with Reliable and Safe
- New materials for strategic use of minor chemical elements

Nanotechnology

Advanced common technologies

- Materials Analysis
- Simulation
- Design and Synthesis

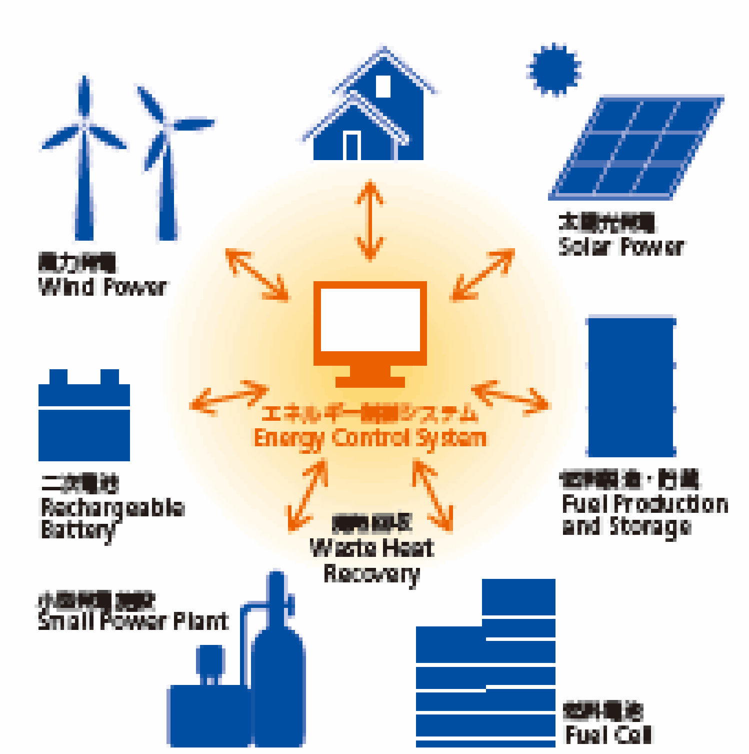
Nano-scale materials

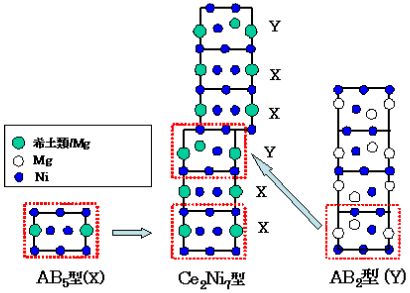
- Material Synthesis in nanoscale
- Nanoscale system optimized for emerging novel property

Material for Power Generation and Storage

Nd,Dy

La,Ce,Pr





La, Ce

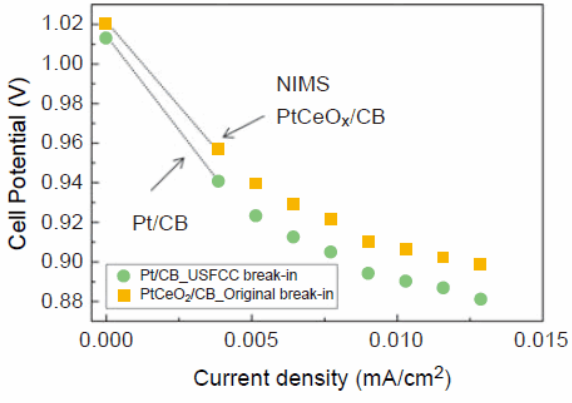
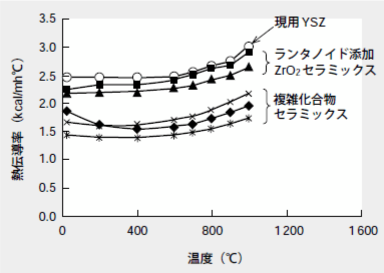


Fig.1 Comparison of generating performance using a NIMS-developed Pt-ceria cathode and an commercial Pt cathode.

Ce,Gd



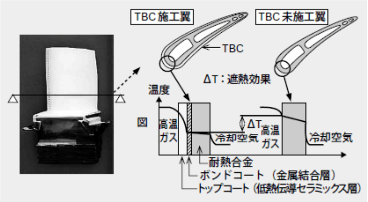
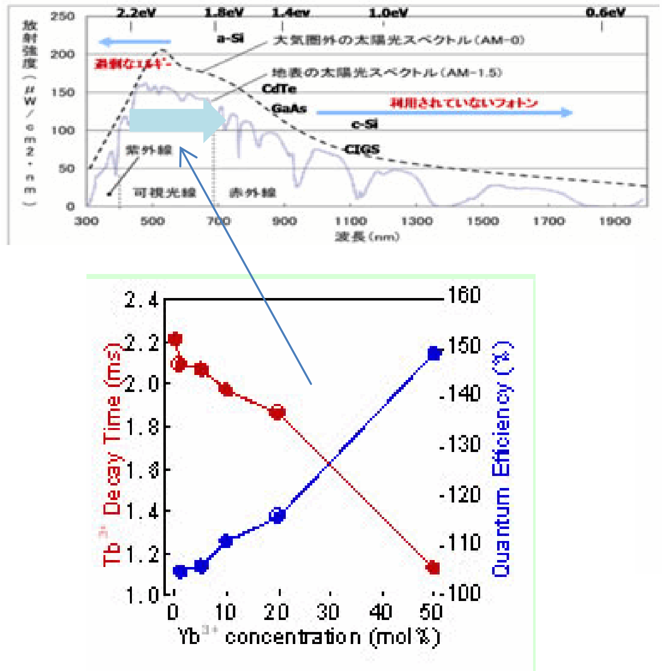
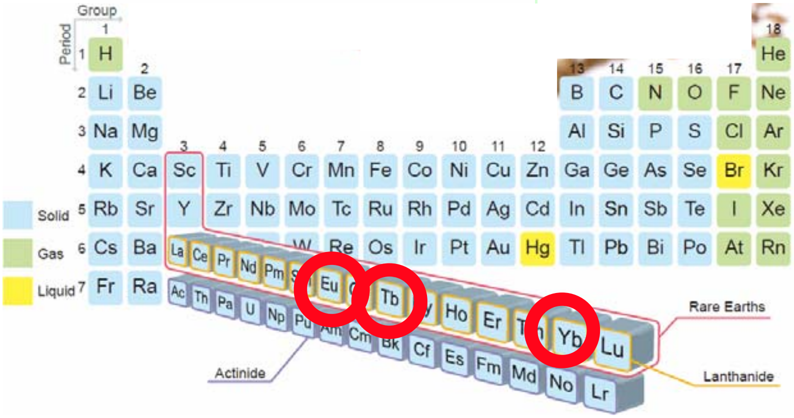


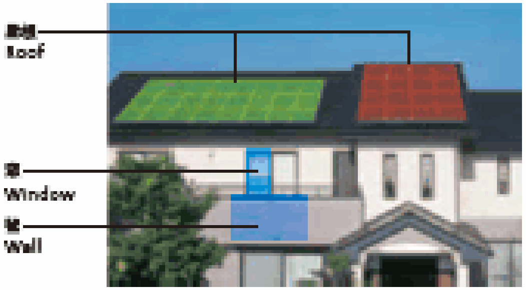
図12　TBCの遮熱効果

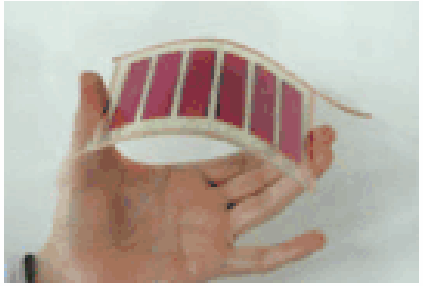
Y,La,Gd

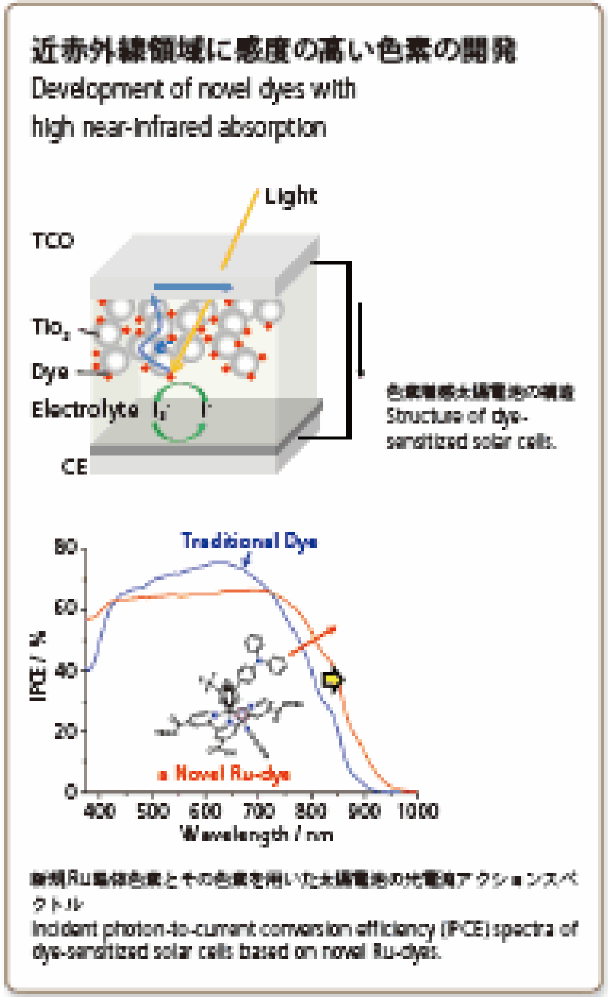
Next generation photovoltaics











近赤外線領域に感度の高い色素の開発

Development of novel dyes with high near-infrared absorption

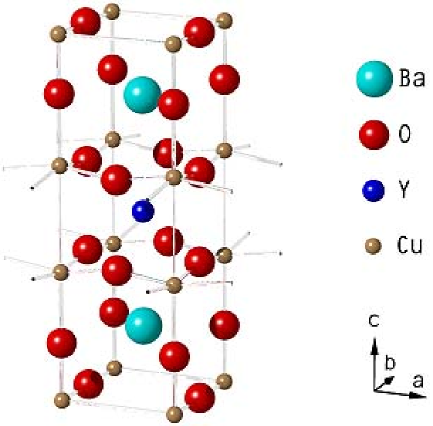
色素増感太陽電池の構造

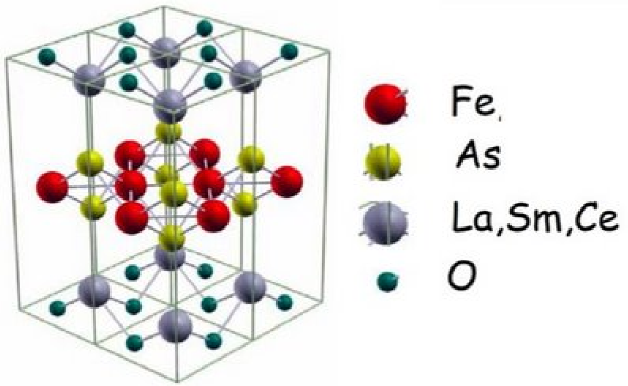
Structure of dye-sensitized solar cells.

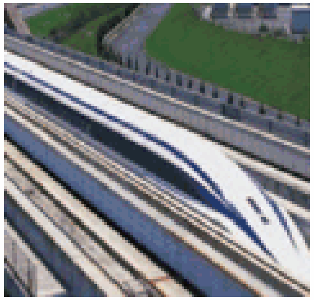
新規Ru錯体色素とその色素を用いた太陽電池の光電流アクションスペクトル

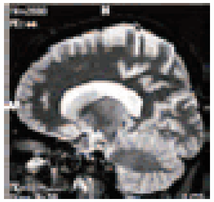
Incident photon-to-current conversion efficiency (IPCE) spectra of dye-sensitized solar cells based on novel Ru-dyes.

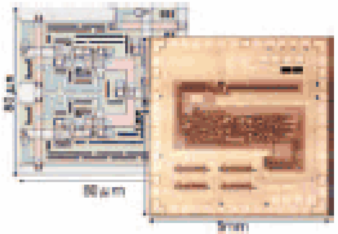
Basic Research on Superconductive towards energy saving

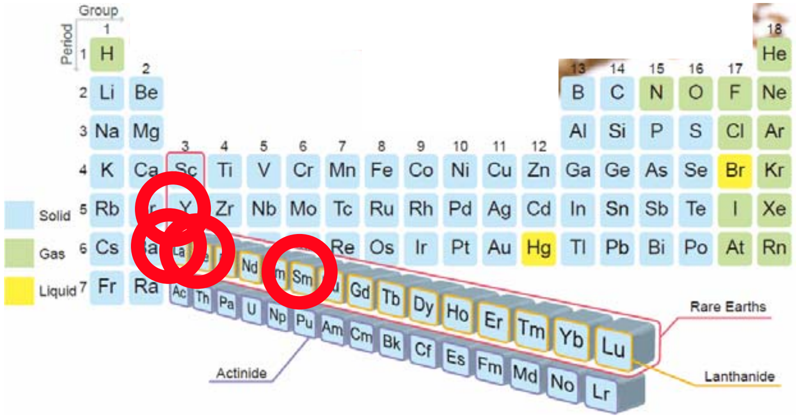


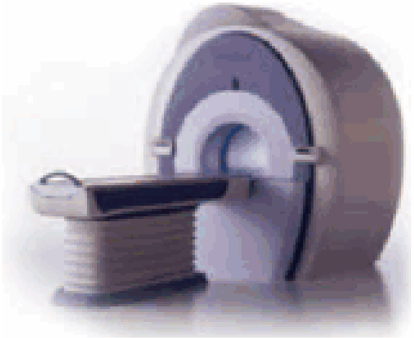












Next-Generation Refrigeration “Magnetic Refrigeration”

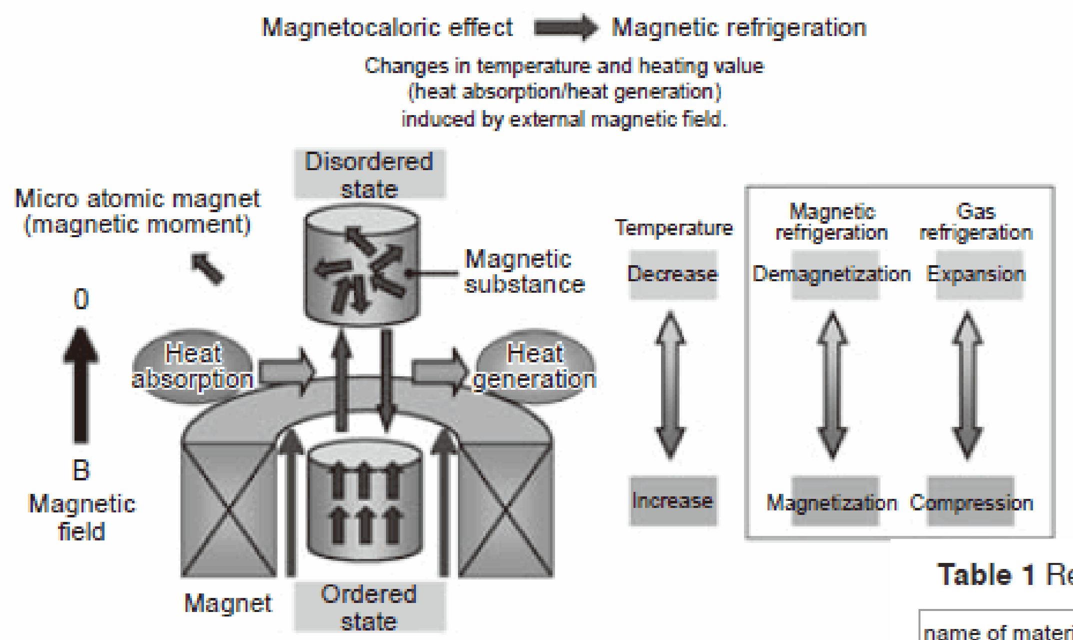


Fig.1 Principle of the magnetocaloric effect

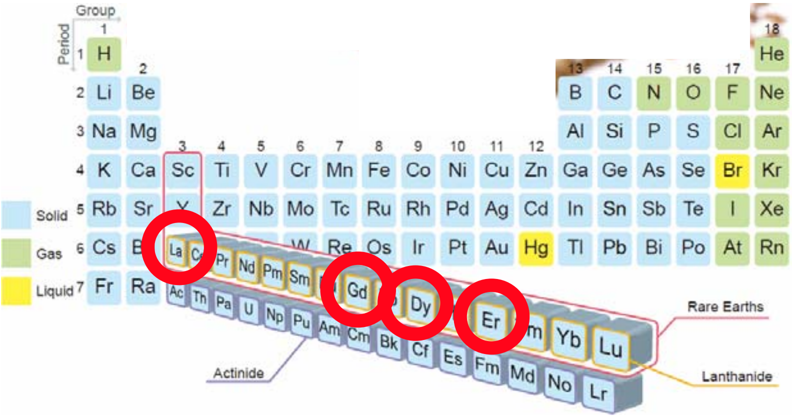
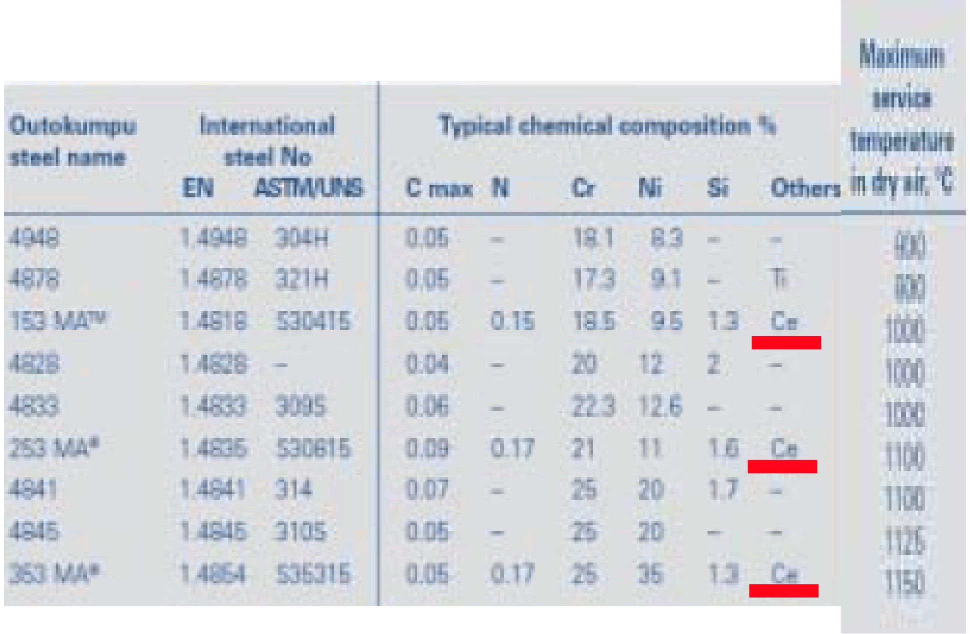


Table 1 Representative examples of magnetic refrigeration materials.

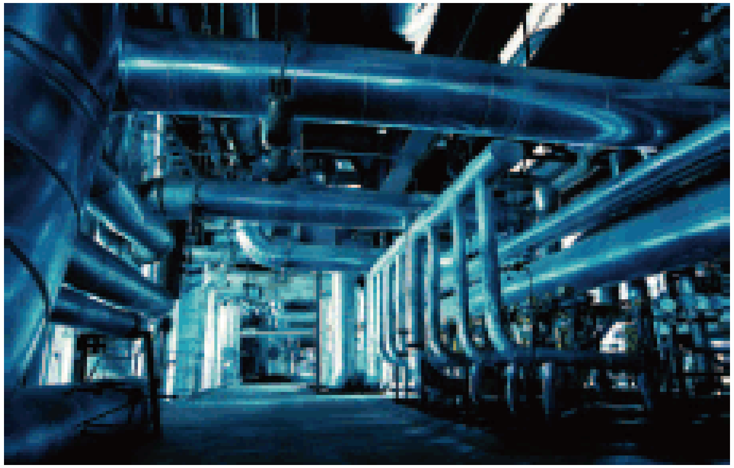
name of material (= Abbreviation)	Magnetic transition temperature	Refrigeration cycle
$CrK(SO_4)_2 \cdot 12H_2O$=CPA	0.009	Carnot
$FeNH_4(SO_4)_2 \cdot 12H_2O$=FAA	0.026	Carnot
$Gd_3Ga_5O_{12}$=GGG	0.85*	Carnot
$Dy_3Al_5O_{12}$=DAG	2.4	Carnot
$ErAl_2$	12	AMR
GdPd	38	AMR
$DyAl_2$	63	AMR
$GdNi_2$	71	AMR
$Gd_5Si_{0.9}Ge_{3.1}$	120	AMR
$Gd_5Si_2Ge_2$	260	AMR
Gd	293	AMR
$La(Fe_xSi_{01-x})_{13}H_y$	280	AMR
MnAs	315	AMR

New materials enable more efficient use of thermal energy

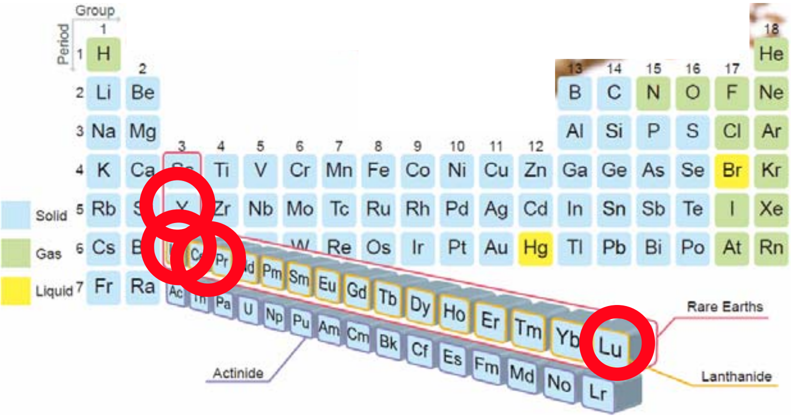


Outokumpu steel name	International steel No		Typical chemical composition %						Maximum service temperature in dry air, °C
	EN	ASTM/UNS	C max	N	Cr	Ni	Si	Others	
4948	1.4948	304H	0.05	–	18.1	8.3	–	–	800
4878	1.4878	321H	0.05	–	17.3	9.1	–	Ti	850
153 MA™	1.4818	S30415	0.05	0.15	18.5	9.5	1.3	Ce	1000
4828	1.4828	–	0.04	–	20	12	2	–	1000
4833	1.4833	309S	0.06	–	22.3	12.6	–	–	1000
253 MA®	1.4835	S30815	0.09	0.17	21	11	1.6	Ce	1100
4841	1.4841	314	0.07	–	25	20	1.7	–	1100
4845	1.4845	310S	0.05	–	25	20	–	–	1125
353 MA®	1.4854	S35315	0.05	0.17	25	35	1.3	Ce	1150

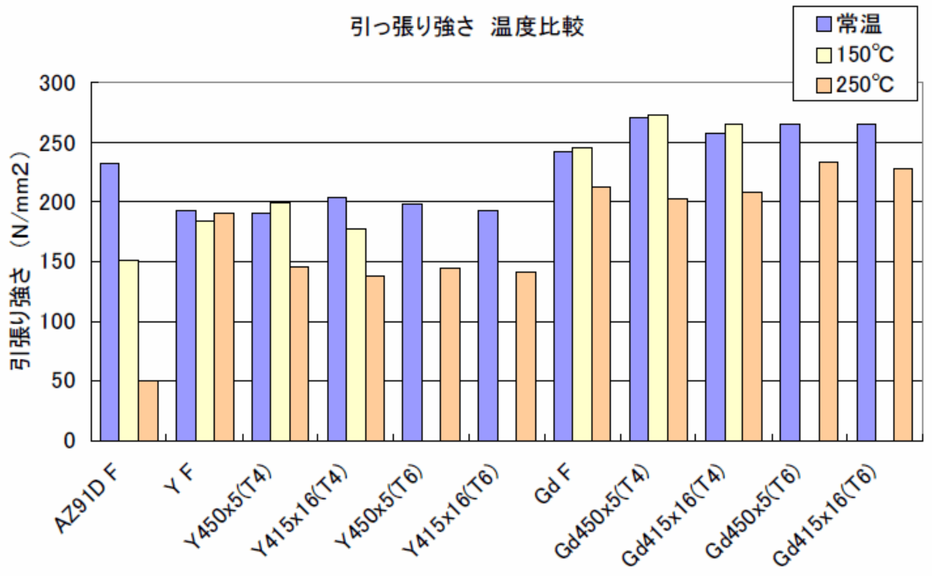
航空機用ジェットエンジン
Jet engine



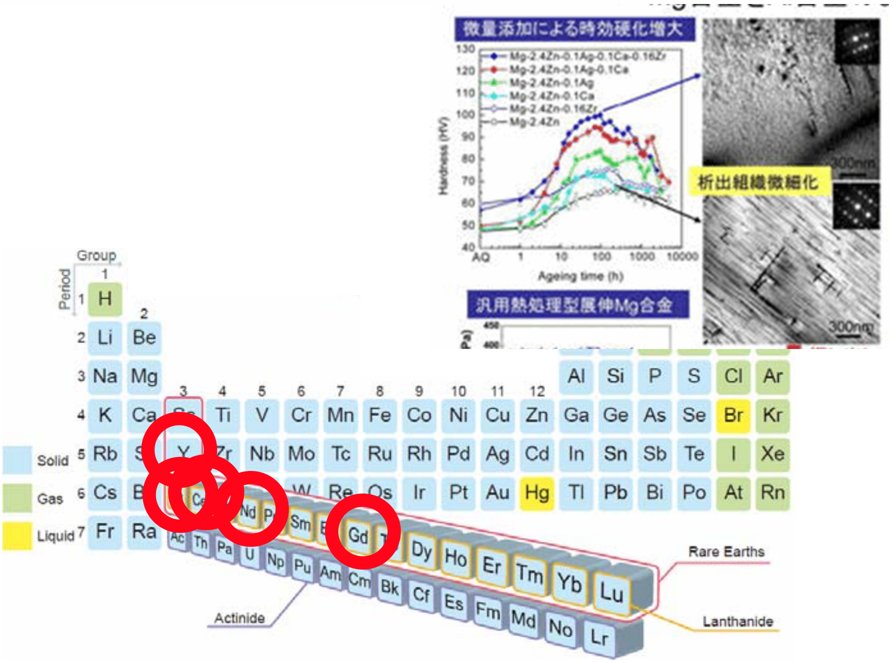
発電プラント
Power Plant



Light-weight high-performance hybrid materials



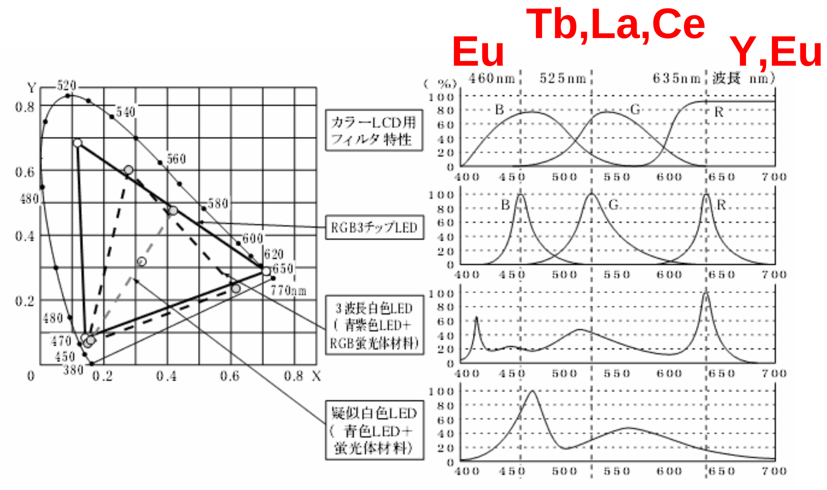
新しいコンセプトに基づく高信頼性自動車
New concept for high reliable automobiles



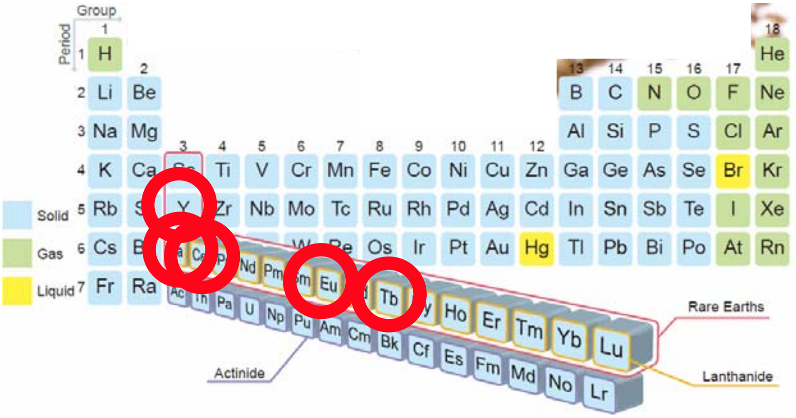
1 試験前
before testing
2 試験後（従来）
after testing
(conventional hybrid)
3 試験後（開発品）
after testing
(developed hybrid)

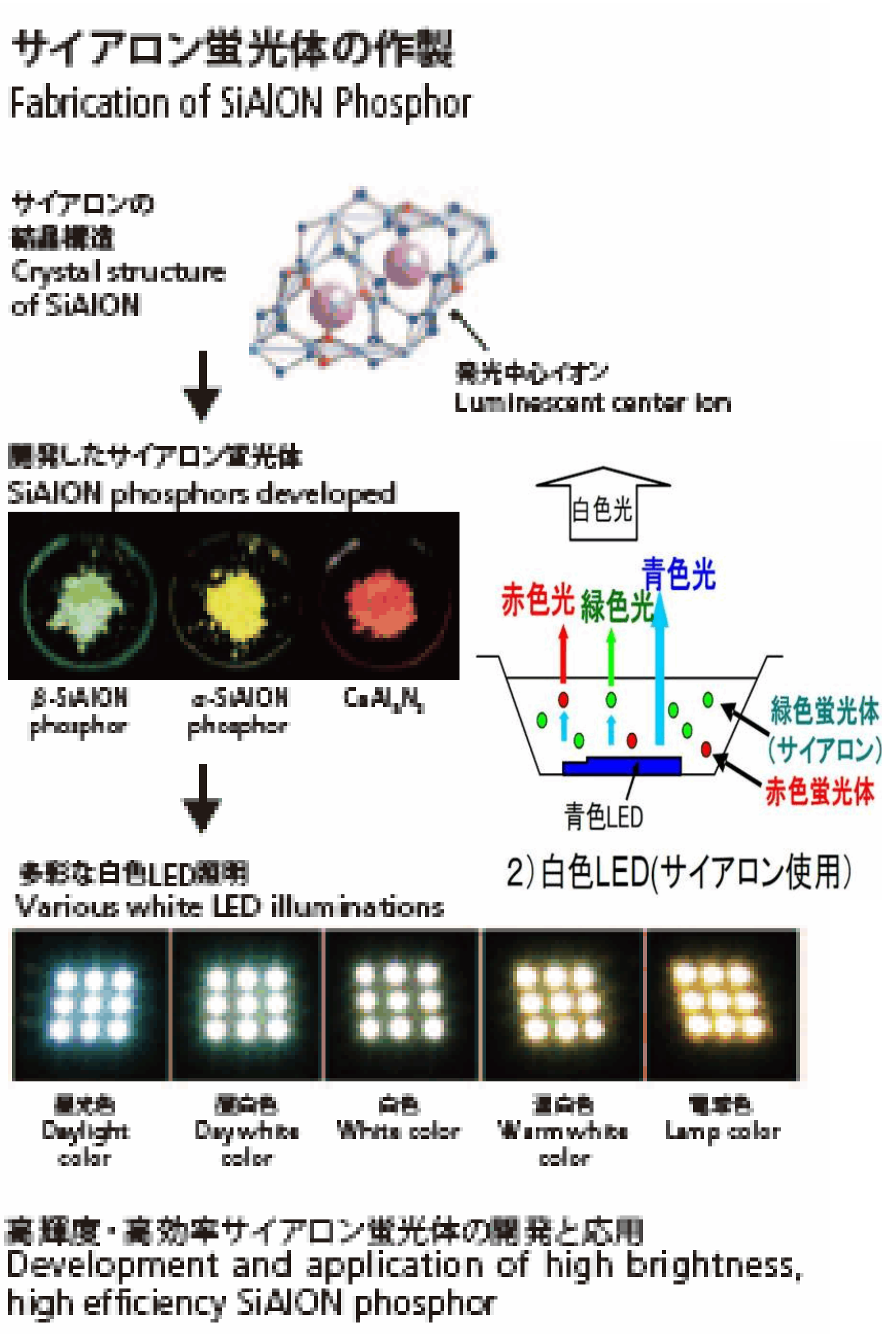
界面性状制御により、破壊（衝撃）エネルギー吸収能力の高い複合材料を実現
Composite materials with high fracture (impact) energy absorbing will be developed by the interface (strength/shape, etc.) control.

Wide-band-gap materials for optics and electronics

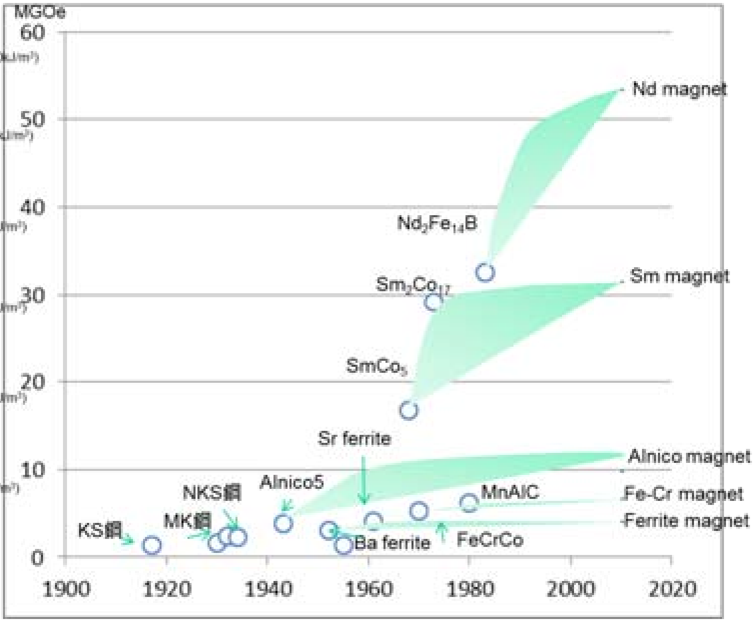


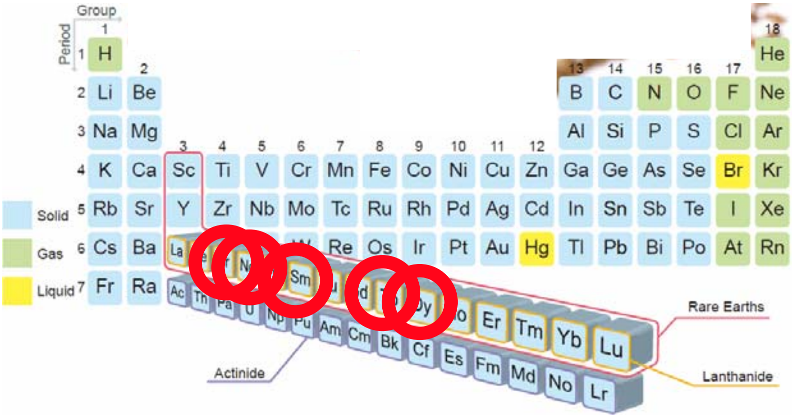
〈図1-A〉 色度図とLEDのタイプ別スペクトル特性

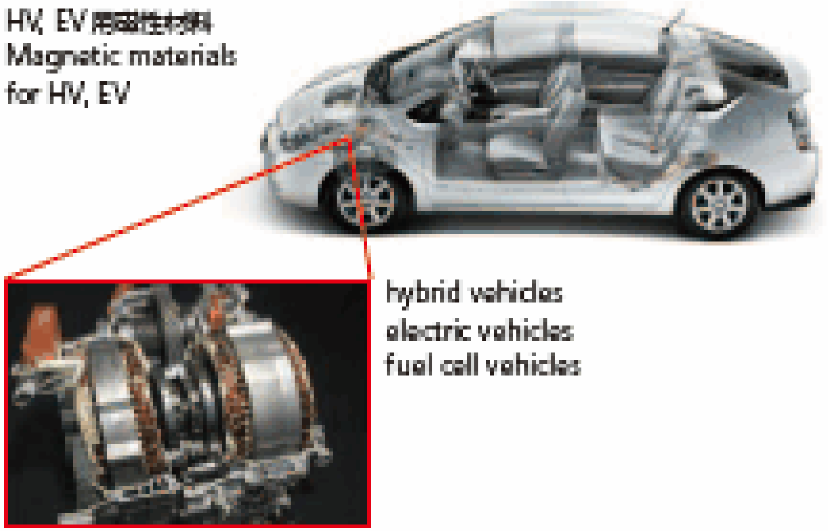




Energy efficient Magnetic Material



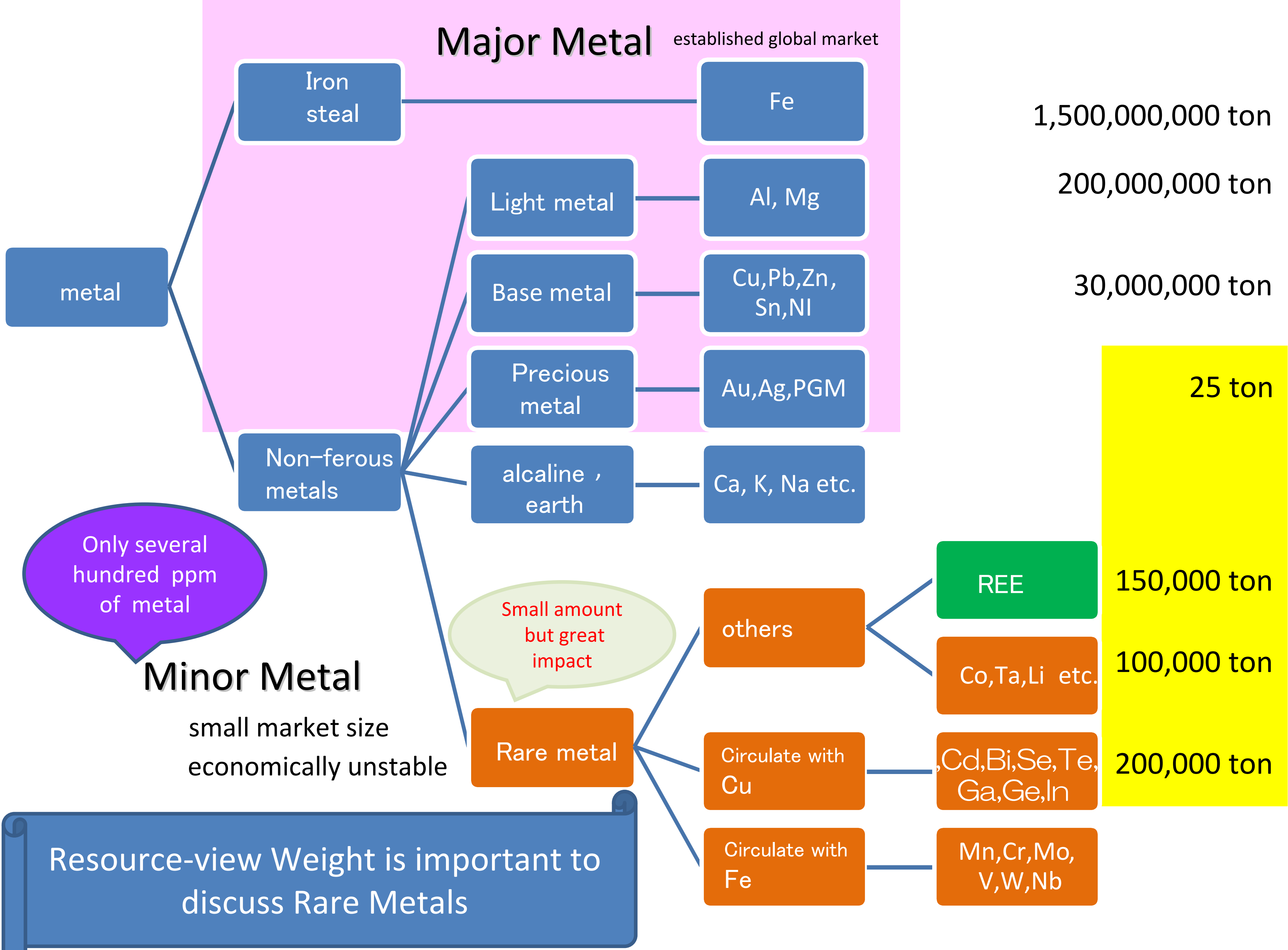




HV, EV 用磁性材料
Magnetic materials
for HV, EV

hybrid vehicles
electric vehicles
fuel cell vehicles

HDD



Major Metal

established global market

- metal
  - Iron steal — Fe — 1,500,000,000 ton
  - Non-ferous metals
    - Light metal — Al, Mg — 200,000,000 ton
    - Base metal — Cu,Pb,Zn, Sn,NI — 30,000,000 ton
    - Precious metal — Au,Ag,PGM — 25 ton
    - alcaline , earth — Ca, K, Na etc.
    - Rare metal
      - others
        - REE — 150,000 ton
        - Co,Ta,Li etc. — 100,000 ton
      - Circulate with Cu — ,Cd,Bi,Se,Te, Ga,Ge,In — 200,000 ton
      - Circulate with Fe — Mn,Cr,Mo, V,W,Nb

Only several hundred ppm of metal

Small amount but great impact

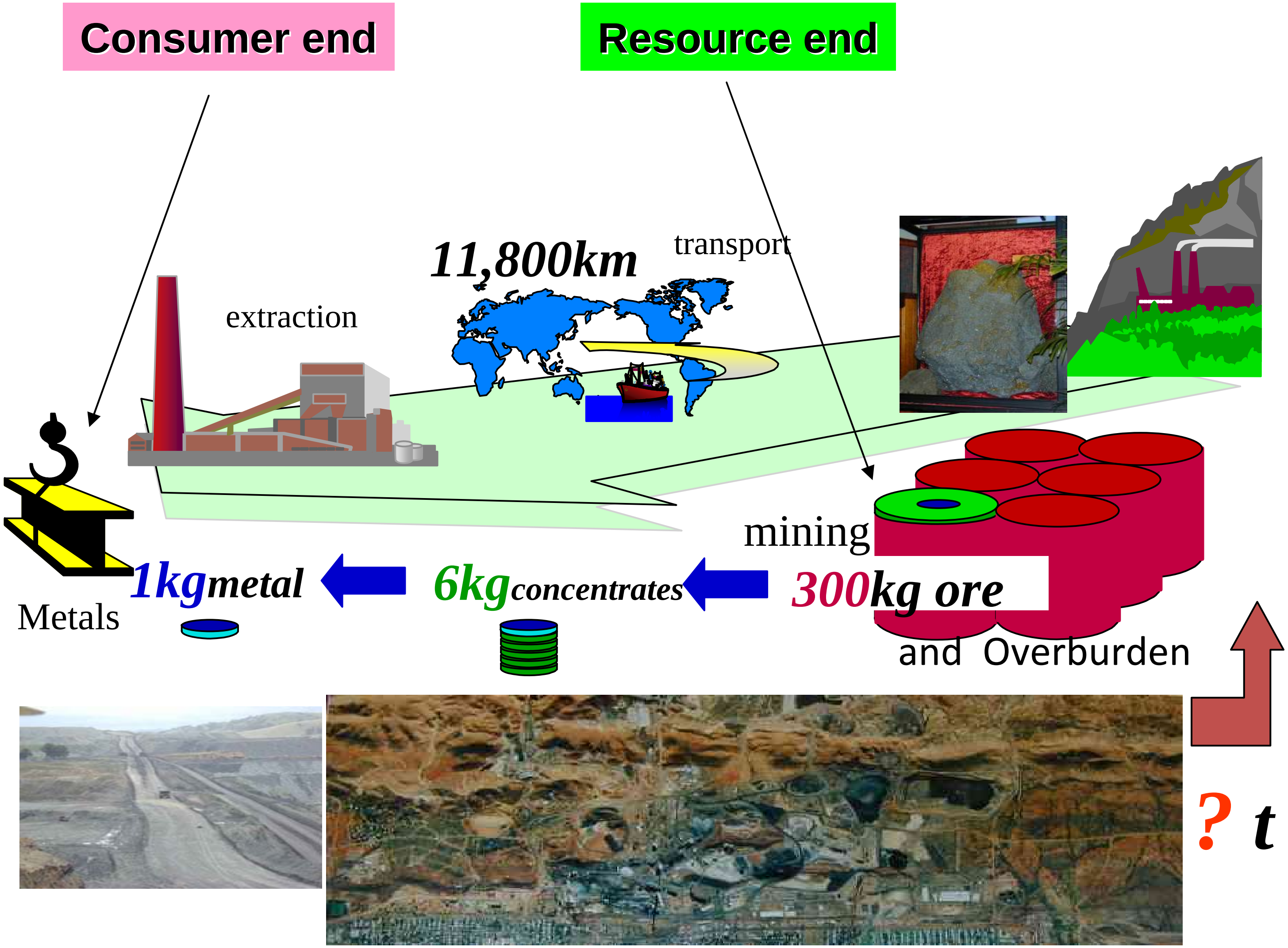
Minor Metal

small market size

economically unstable

Resource-view Weight is important to discuss Rare Metals

Resource(-end)-view weight



Consumer end

Resource end

extraction

11,800km transport

mining

***1kg**metal*

***6kg**concentrates*

***300**kg ore*

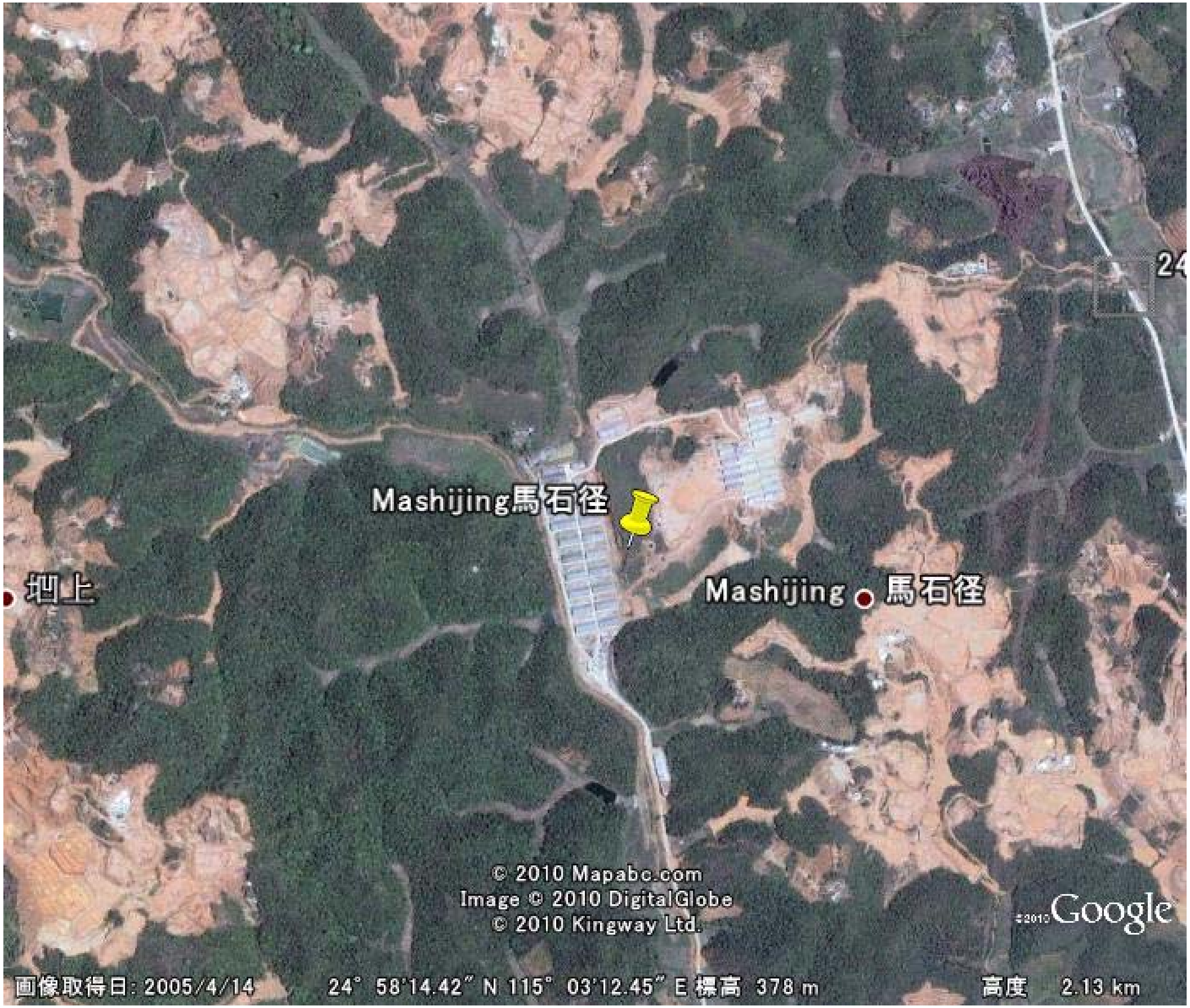
and Overburden

Metals

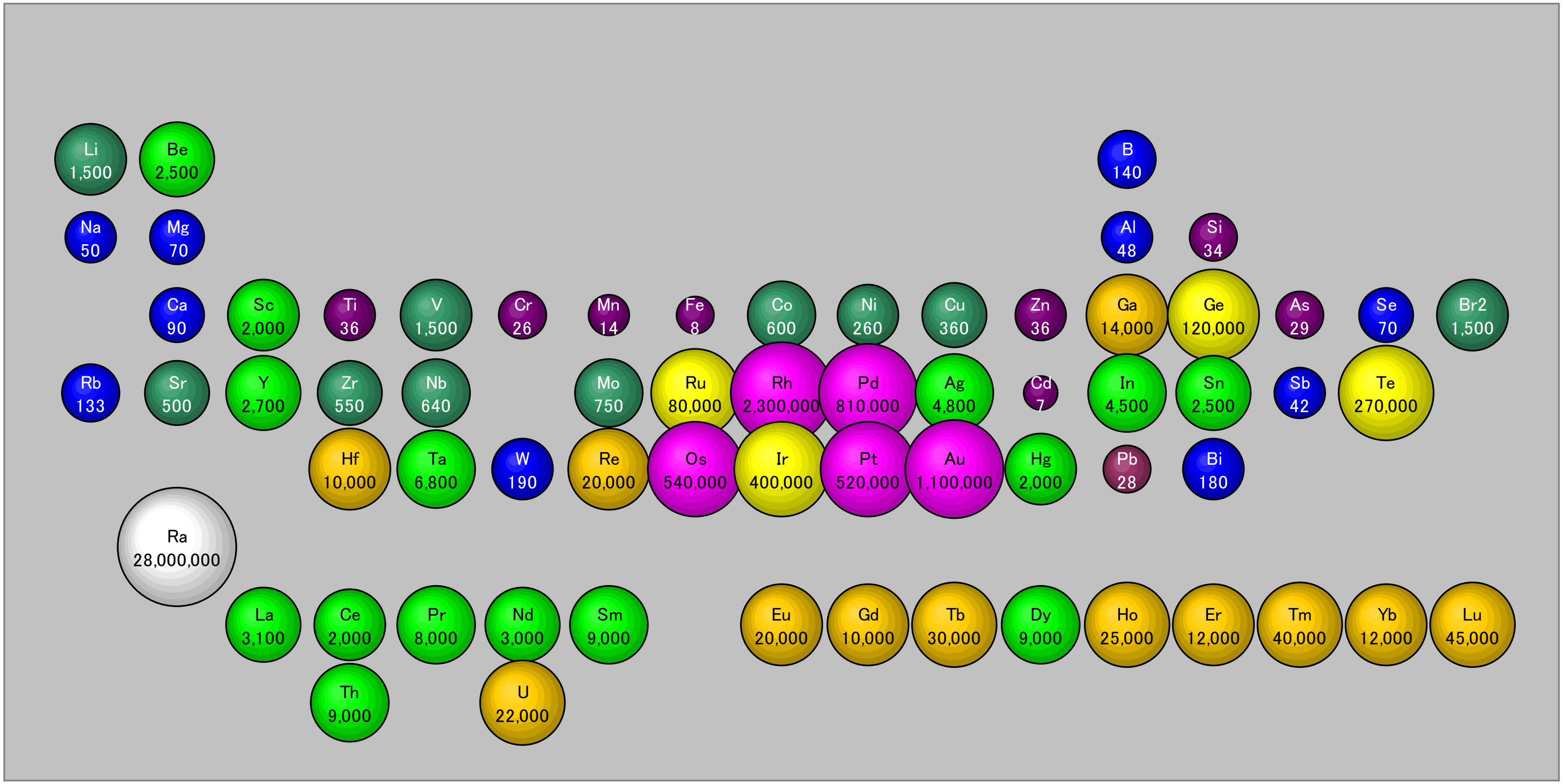
? t

TMR: Total Materials Requirements, or Ecological rucksacks

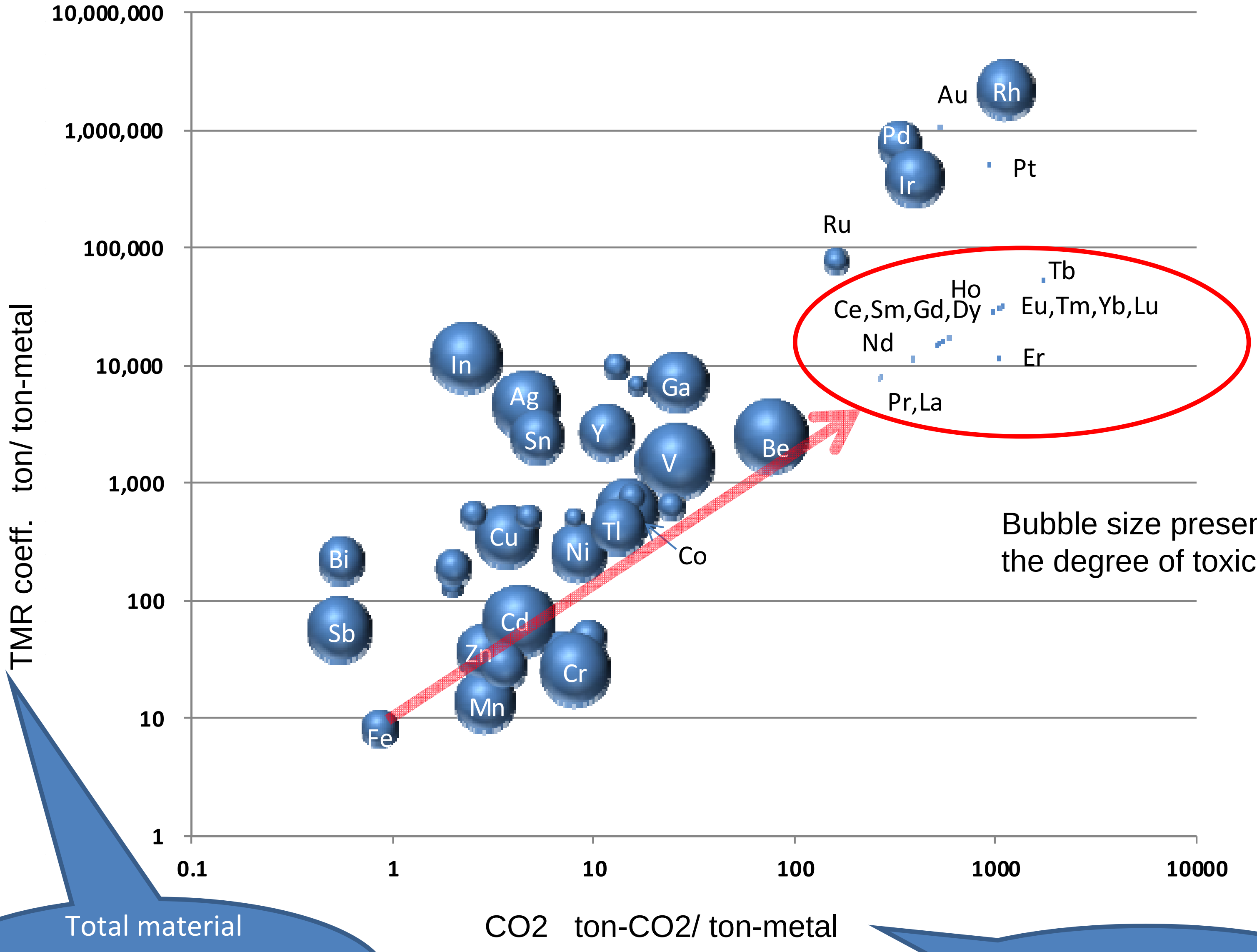
Photo by Taniguchi


24
Mashijing馬石径
垇上
Mashijing 馬石径
© 2010 Mapabc.com
Image © 2010 DigitalGlobe
© 2010 Kingway Ltd.
©2010 Google
画像取得日: 2005/4/14
24° 58'14.42" N 115° 03'12.45" E 標高 378 m
高度 2.13 km

TMR coefficients of metals
(size of the bubble is proportional to the digit number)



1kg R.E.E. is nearly equivalent to 1 ton Fe by environmental view

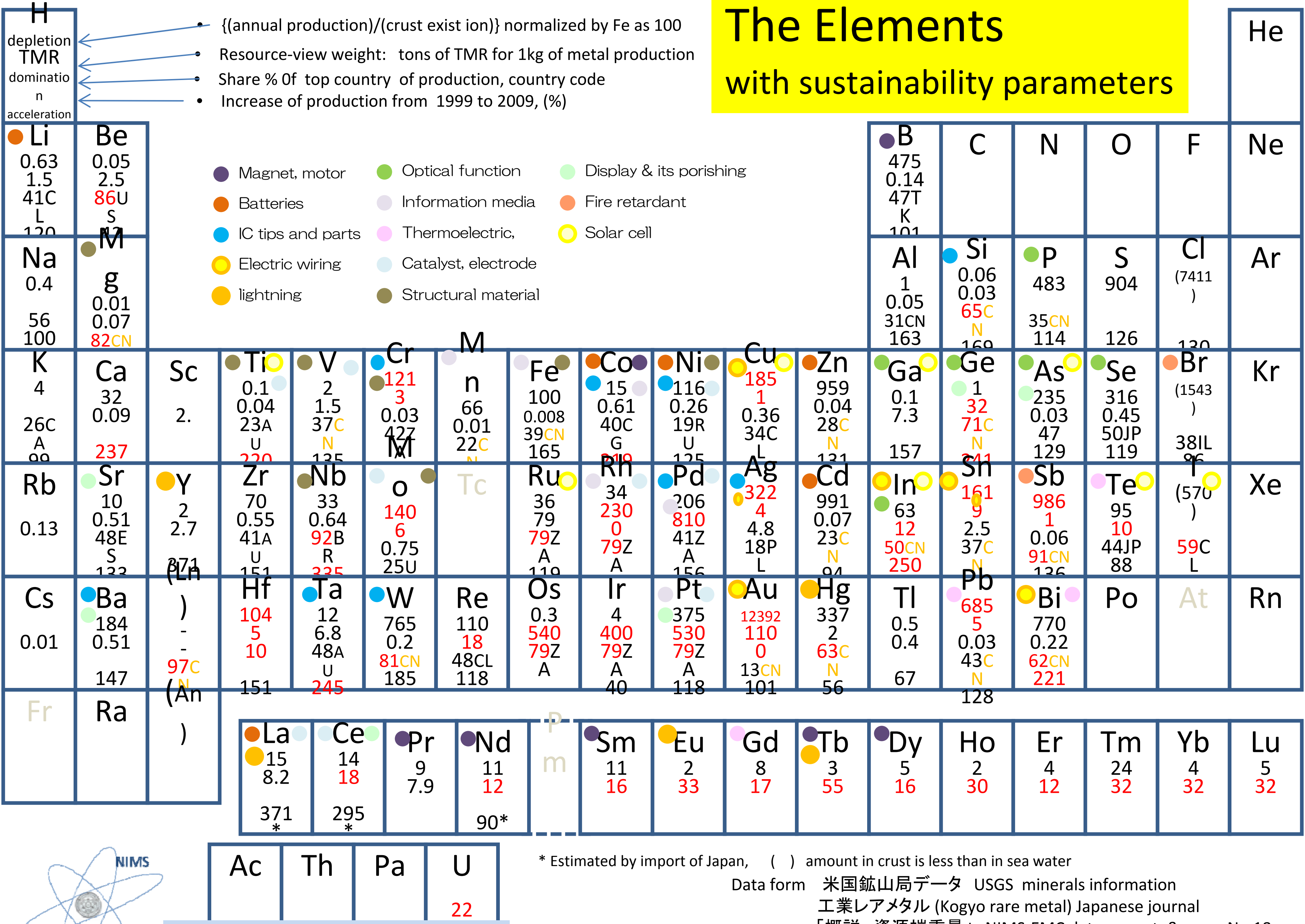


Bubble size presents
the degree of toxicity

Total material
requirement
≈
Waist from mining

CO2 emission during
mining and extraction

The Elements
with sustainability parameters



- {(annual production)/(crust exist ion)} normalized by Fe as 100
- Resource-view weight: tons of TMR for 1kg of metal production
- Share % 0f top country of production, country code
- Increase of production from 1999 to 2009, (%)

● Magnet, motor
● Batteries
● IC tips and parts
● Electric wiring
● lightning
● Optical function
● Information media
● Thermoelectric,
● Catalyst, electrode
● Structural material
● Display & its porishing
● Fire retardant
● Solar cell

H depletion TMR domination acceleration																	He
Li 0.63 1.5 41CL 120	Be 0.05 2.5 86US 47											B 475 0.14 47TK 101	C	N	O	F	Ne
Na 0.4 56 100	Mg 0.01 0.07 82CN											Al 1 0.05 31CN 163	Si 0.06 0.03 65CN 169	P 483 35CN 114	S 904 126	Cl (7411) 130	Ar
K 4 26CA 99	Ca 32 0.09 237	Sc 2.	Ti 0.1 0.04 23AU 220	V 2 1.5 37CN 135	Cr 1213 0.03 427	Mn 66 0.01 22CN	Fe 100 0.008 39CN 165	Co 15 0.61 40CG 219	Ni 116 0.26 19RU 125	Cu 1851 0.36 34CL	Zn 959 0.04 28CN 131	Ga 0.1 7.3 157	Ge 1 32 71CN 241	As 235 0.03 47 129	Se 316 0.45 50JP 119	Br (1543) 38IL 86	Kr
Rb 0.13	Sr 10 0.51 48ES 133	Y 2 2.7 371	Zr 70 0.55 41AU 151	Nb 33 0.64 92BR 335	Mo 1406 0.75 25U	Tc	Ru 36 79 79ZA 119	Rh 34 2300 79ZA	Pd 206 810 41ZA 156	Ag 3224 4.8 18PL	Cd 991 0.07 23CN 94	In 63 12 50CN 250	Sn 1619 2.5 37CN	Sb 9861 0.06 91CN 136	Te 95 10 44JP 88	I (570) 59CL	Xe
Cs 0.01	Ba 184 0.51 147	(Ln) - - 97CN	Hf 1045 10 151	Ta 12 6.8 48AU 245	W 765 0.2 81CN 185	Re 110 18 48CL 118	Os 0.3 540 79ZA	Ir 4 400 79ZA 40	Pt 375 530 79ZA 118	Au 12392 1100 13CN 101	Hg 337 2 63CN 56	Tl 0.5 0.4 67	Pb 6855 0.03 43CN 128	Bi 770 0.22 62CN 221	Po	At	Rn
Fr	Ra	(An)															
			La 15 8.2 371*	Ce 14 18 295*	Pr 9 7.9	Nd 11 12 90*	Pm	Sm 11 16	Eu 2 33	Gd 8 17	Tb 3 55	Dy 5 16	Ho 2 30	Er 4 12	Tm 24 32	Yb 4 32	Lu 5 32
			Ac	Th	Pa	U 22											

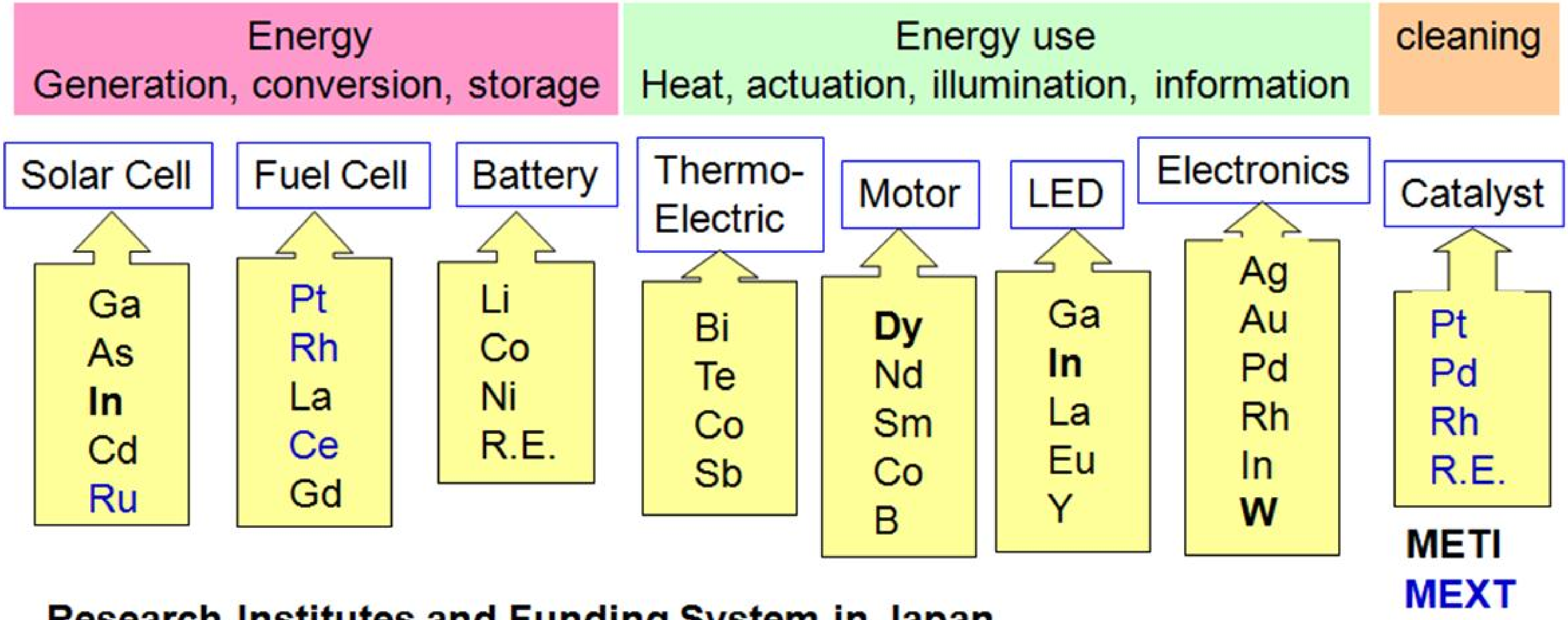
NIMS
元素戦略センター

http://www.nims.go.jp/genso/

* Estimated by import of Japan, ( ) amount in crust is less than in sea water

Data form 米国鉱山局データ USGS minerals information
工業レアメタル (Kogyo rare metal) Japanese journal
「概説 資源端重量」 NIMS-EMC data on mat. & env. No.18
Halada, Katagiri, Proc. of EcoBalance 2010 p609

Critical Elements for Energy and Environment



Energy
Generation, conversion, storage

Energy use
Heat, actuation, illumination, information

cleaning

Solar Cell: Ga, As, **In**, Cd, Ru

Fuel Cell: Pt, Rh, La, Ce, Gd

Battery: Li, Co, Ni, R.E.

Thermo-Electric: Bi, Te, Co, Sb

Motor: **Dy**, Nd, Sm, Co, B

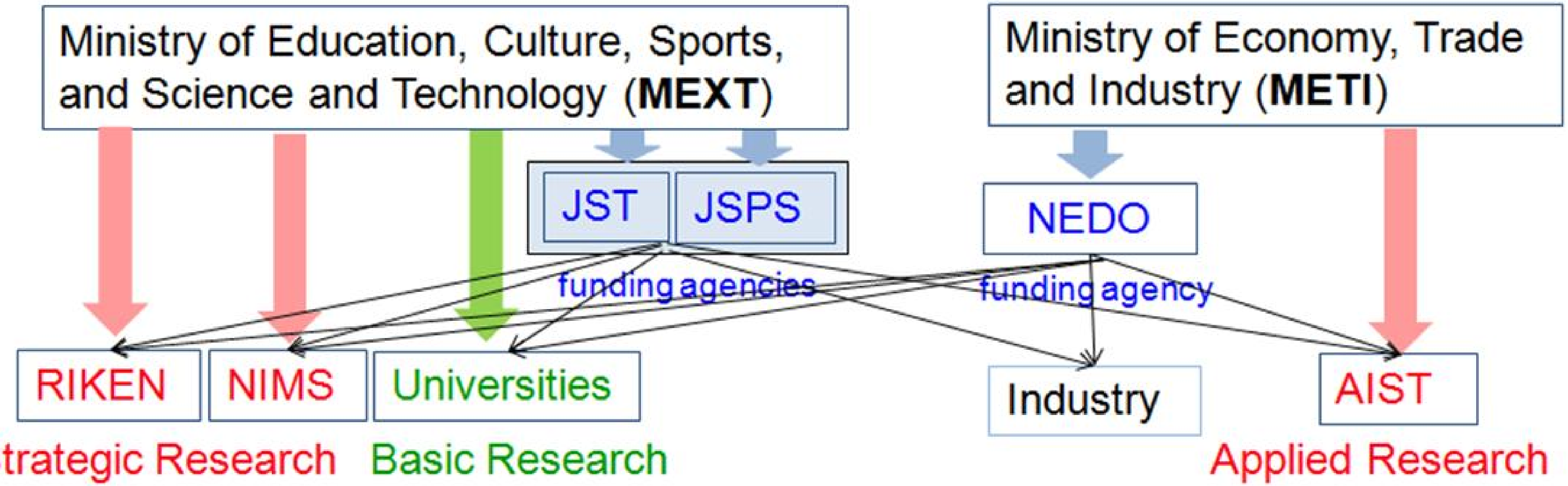
LED: Ga, **In**, La, Eu, Y

Electronics: Ag, Au, Pd, Rh, In, **W**

Catalyst: Pt, Pd, Rh, R.E.

METI
MEXT

Research Institutes and Funding System in Japan



Ministry of Education, Culture, Sports, and Science and Technology (**MEXT**)

Ministry of Economy, Trade and Industry (**METI**)

JST
JSPS
funding agencies

NEDO
funding agency

RIKEN
NIMS
Universities
Industry
AIST

Strategic Research
Basic Research
Applied Research

MEXT

Elements Science and Technology Project

- Designing Material Functions through Fundamental Research on Elements' Roles

GENSO SENRYAKU

started 2007

An elemental strategy projec

Background

Rare earths and other **rare metals** utilized for electronics, automotives, information technologies, and robotics are facing their price increase and tight supply due to the rapid increase of their consumptions and export policies of producing countries.

Project Outline

Establish sciences on the roles of critical elements in materials to use alternative elements

R&D Aspects on Research Subjects

1. Alternative materials composed of ubiquitous and nonhazardous elements
2. Advanced utilization of functions stemming from strategic elements
3. Practical material design for the effective use of strategic elements

METI also started **Rare Metal Substitution Project** in 2007

THREE APPROACHES OF ELEMENTS SCIENCE AND TECHNOLOGY PROJECT

started 2007

Approach of Minimization:

Material design of higher resource efficiency, namely reduction in quantity per function, is expected as immediate measure. Nano-technology is powerful in this approach

Approach of Substitution to more abundant element:

Material design with nano-technology has the possibility of functional design with other chemicals and elements. Band gap design electron orbit design with nano-technology give us various possibility

Approach of Circulation:

Japan has a great possibility of urban mining. Nano-technologies such as molecular identification expected to provide new tool to selective concentration from waste,

Sialon Fluorescent Material with High Brightness and High Efficiency

Research impact

Durable phosphors have been developed by introducing the luminescent ions such as Eu into the crystal of SiAlONs.

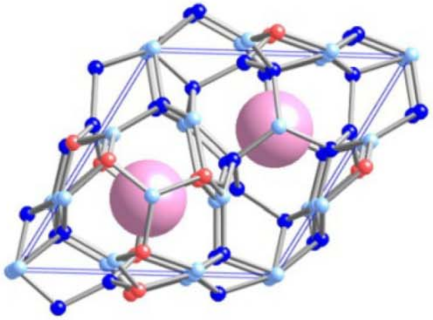


Fig.1 SiAlON crystals

Fig.2 SiAlON Phosphor

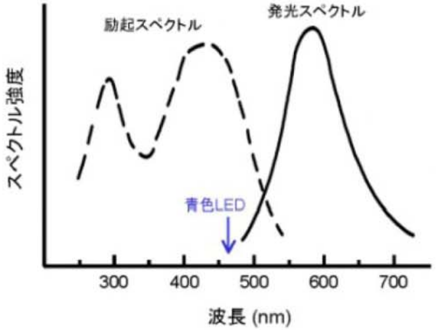


Fig. 3 Luminescence property

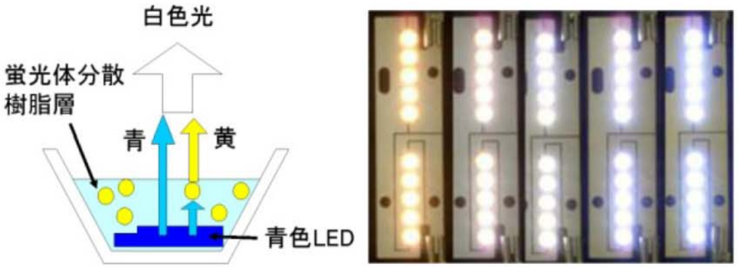


Fig.4 Principle of white LED

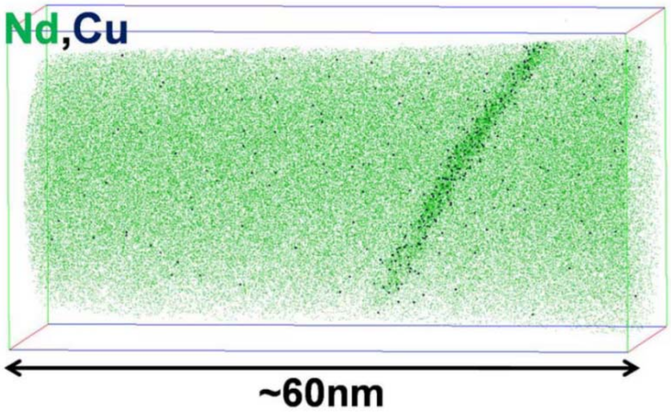
- **Superior to durability and high temperature stability**
- **Excitation by blue LED**

minimization

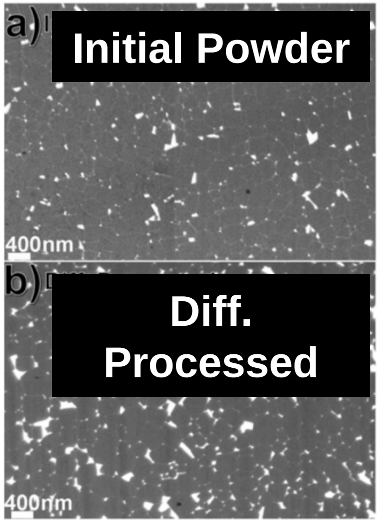
Neodymium Magnet without Dysprosium

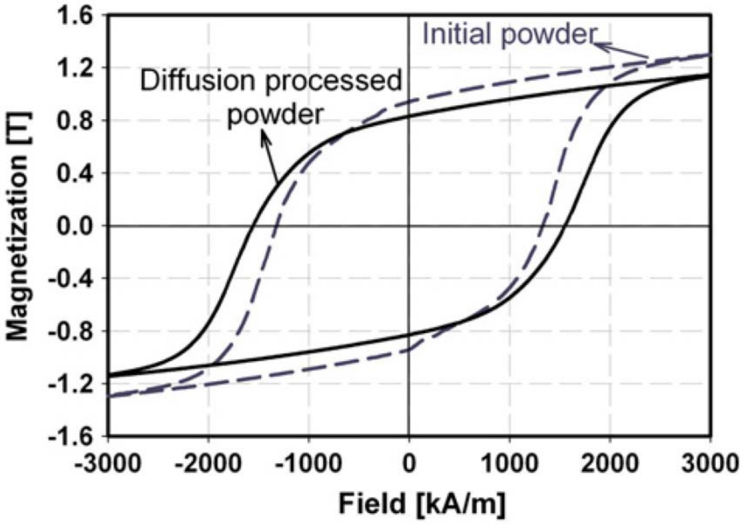
Research impact

- **A method for increasing the coercivity of neodymium magnet powder without using dysprosium**
- **Thickening of the Nd-rich grain boundary phase could be attributed to the coercivity enhancement.**



3DAP map of Nd and Cu of the diffusion processed sample

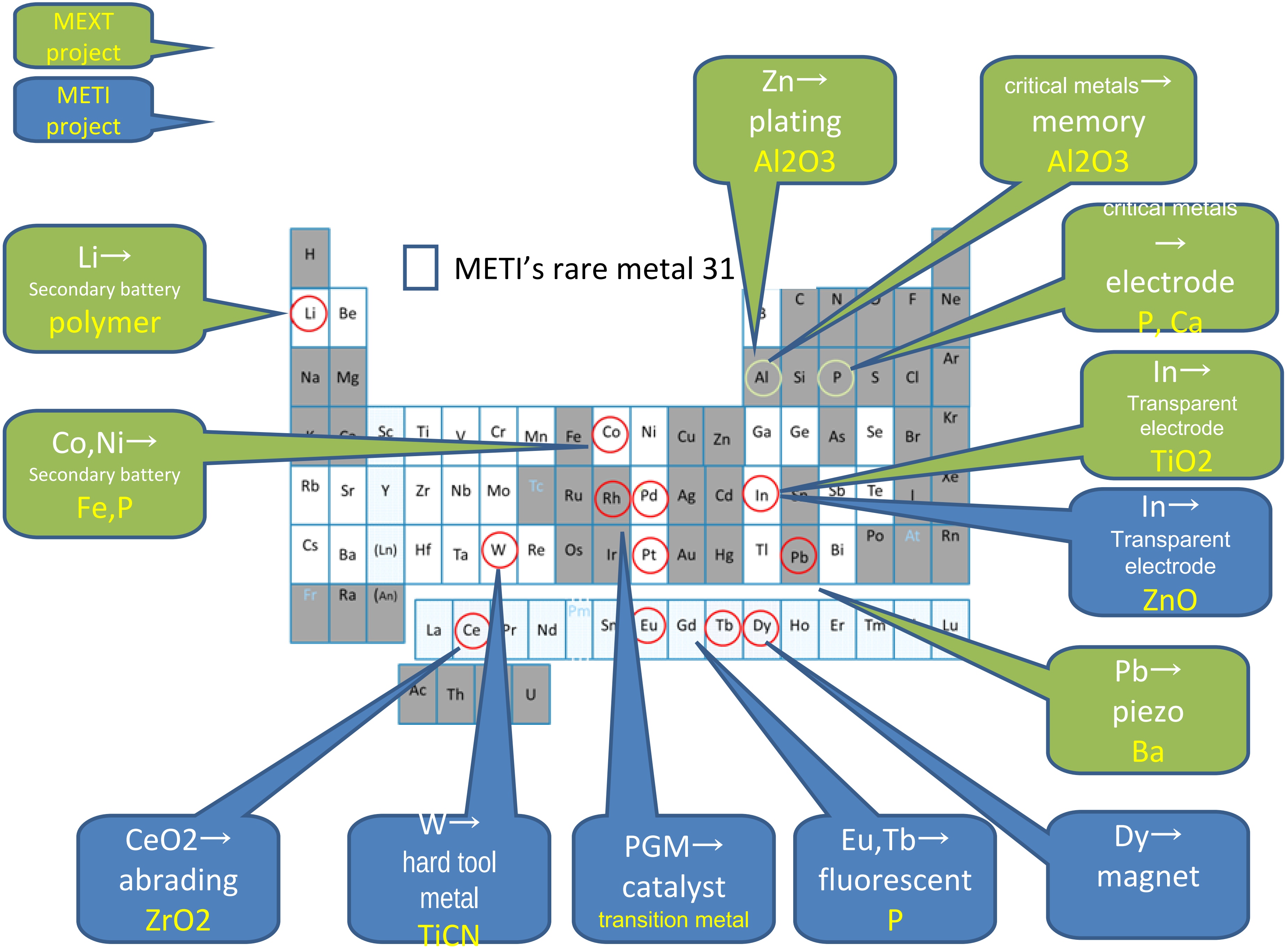




- The systematic nanostructure analysis of existing neodymium magnets using 3D Atom Probe reveals that the coercivity can be improved by decoupling the ferromagnetic interactions between the crystal grains.

REE free

Scripta Materialia, 63, 1124 (2010)



MEXT project

METI project

☐ METI's rare metal 31

Zn→
plating
Al2O3

critical metals→
memory
Al2O3

critical metals
→
electrode
P, Ca

Li→
Secondary battery
polymer

Co,Ni→
Secondary battery
Fe,P

In→
Transparent electrode
TiO2

In→
Transparent electrode
ZnO

Pb→
piezo
Ba

CeO2→
abrading
ZrO2

W→
hard tool metal
TiCN

PGM→
catalyst
transition metal

Eu,Tb→
fluorescent
P

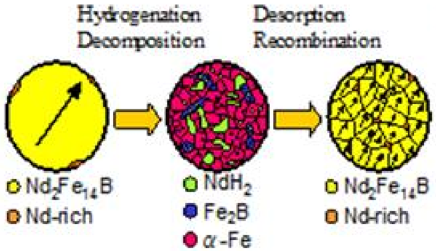
Dy→
magnet

Elements Science and Technology

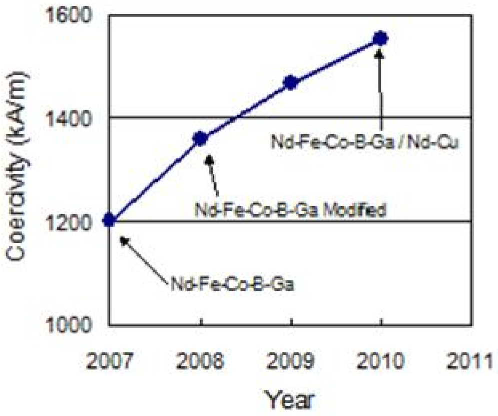
High Performance Anisotropic Nanocomposite Permanent Magnets with Low Rare Earth Content

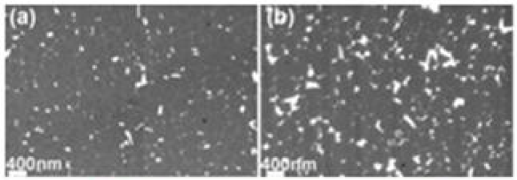
S. Hirosawa, *Hitachi Metals., Ltd.,*
Hitachi Metals, NIMS, Ehime Univ., Kitakyushuu Univ.

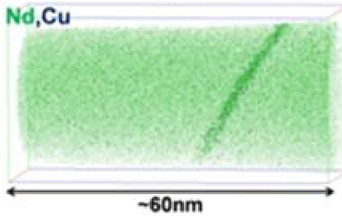
A new category of permanent magnet materials with no Dy and less Nd with comparable magnetic properties with those of current (Nd,Dy)-Fe-B sintered magnets using HDDR (Hydrogenation-Decomposition-Desorption-Recombination) and Fe-nanocoating processes.

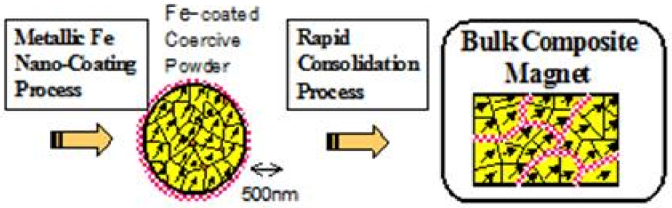


Microstructural Analyses and Grain-Boundary Modification

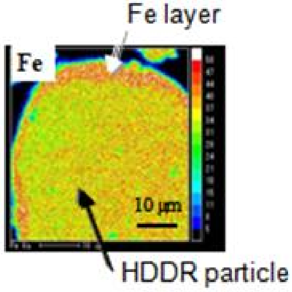




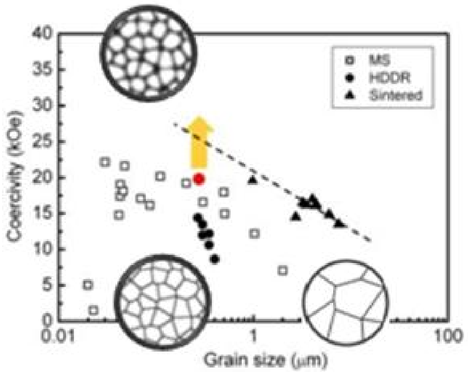




Search of non-aqua coating process on hard-magnetic particles



Concept of the Subjects

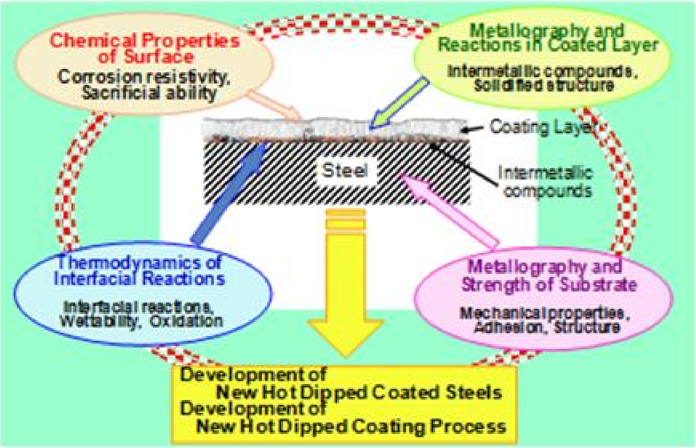


MEXT Elements Science and Technology: Granted in FY2007

Development of Hot-dipped Aluminum Alloy Coated Steels

T. Tsuru, *Tokyo Institute of Technology*

Substitution of **Zn** with Al on Zn coated steel



Chemical Properties of Surface
Corrosion resistivity, Sacrificial ability

Metallography and Reactions in Coated Layer
Intermetallic compounds, Solidified structure

Thermodynamics of Interfacial Reactions
Interfacial reactions, Wettability, Oxidation

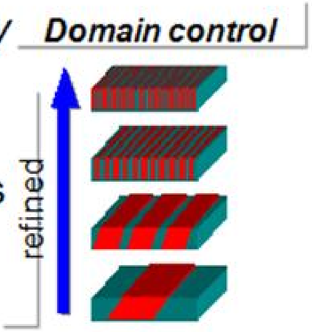
Metallography and Strength of Substrate
Mechanical properties, Adhesion, Structure

Development of New Hot Dipped Coated Steels
Development of New Hot Dipped Coating Process

Development of Barium-based New Lead-free Piezoelectric Materials with Ultrahigh Piezoelectric Property for Piezoelectric Frontier

S. Wada, *Yamanashi University*

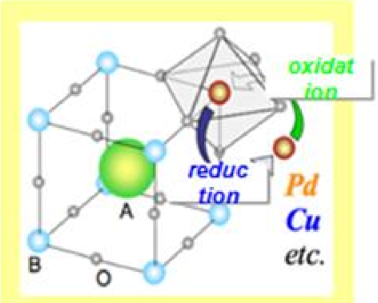
Ba-based new **Pb-free piezoelectric materials** with ultrahigh piezoelectric properties for future automobile MEMS applications.



Self-forming Nano-particle Catalyst without Precious Metals

Y. Nishihata, *Japan Atomic Energy Agency*

Substantial reduction and/or total substitution of the **precious metals** in the automotive catalyst for gasoline engine.

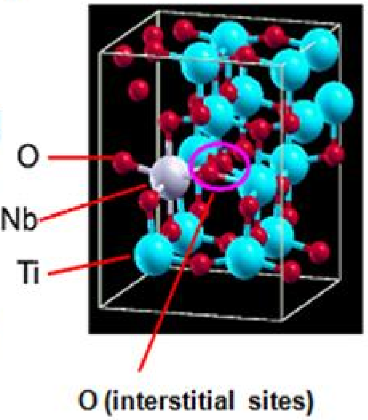


Solution / precipitation
nano recycle

Development of TiO_2-based Transparent Electrode

T. Hasegawa, *Kanagawa Academy of Science and Technology*

As an **ITO** (Indium Tin Oxide) alternative, the sputtering- and CVD (Chemical Vapor Deposition) -based practical processes for fabrication of indium-free TNO (niobium-doped titanium dioxide) transparent conducting thin films will be developed.

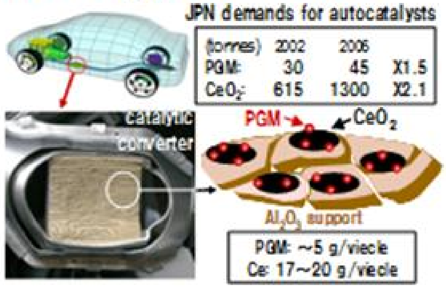


MEXT Elements Science and Technology: Granted in FY2008

Material Design and Processing of Highly-dispersed Catalysts with Minimum Precious Metal Loadings

M. Machida, *Kumamoto University*

Minimizing the loading of precious metals (PGM=**Rh, Pt, Pd**) and rare earth elements (**Ce**) in automotive catalysts by realizing thermally stable and highly dispersed PGM nano-particles anchored onto support surface.



JPN demands for autocatalysts

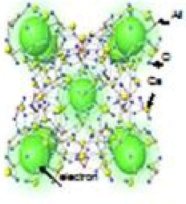
(tonnes)	2002	2006	
PGM:	30	45	X1.5
CeO_2:	615	1300	X2.1

PGM: ~5 g/viecle
Ce: 17~20 g/viecle

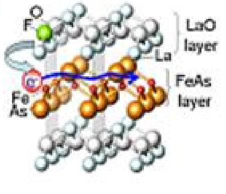
Ubiquitous Element Strategy for Function Emergence

H. Hosono, *Tokyo Institute of Technology*

Novel functionality based on abundant elements utilizing built-in nanostructures, interface/surface and/or defects.



C12A7-Electride



Iron -based superconductor

Nano-hybridized Precious-metal-free Catalysts for Chemical Energy Conversion

K. Uosaki, *Hokkaido University*

Nano-hybridized **precious-metal-free catalysts** for the innovation of fuel cell and photo-electrochemical cell.

Adsorption of hetero-metal complex to electrode surface

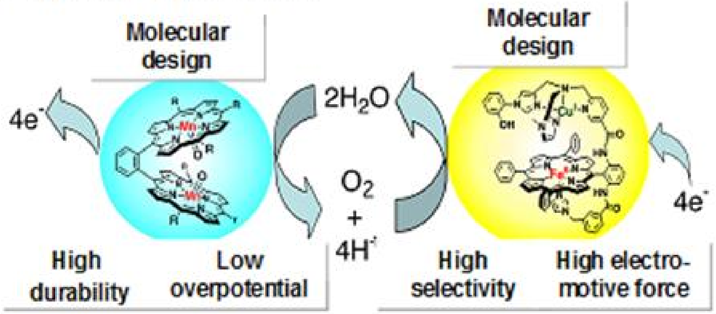
Dissolution & growth

Precipitation of core ions as metal

Development of Innovative Energy Conversion Systems with Molecular Catalysts Replacing Precious Metals

Y. Naruta, *Kyushu University*

Development of **molecular catalysts w/o precious metal ions** for water decomposition to H_2/O_2 as well as O_2 reduction using organic-inorganic hybrid systems.



Molecular design

Molecular design

High durability

Low overpotential

High selectivity

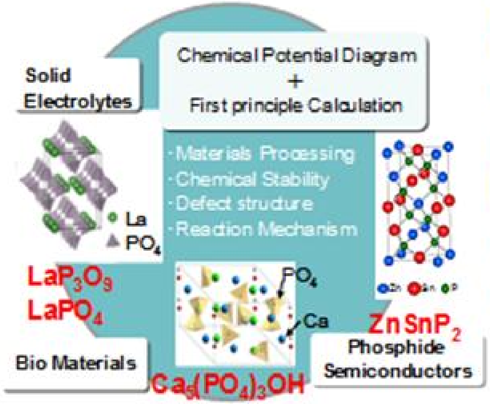
High electro-motive force

MEXT Elements Science and Technolgoy: Granted in FY2009

Design and Processing of Functional Materials with Multi-elements Based on Chemical Potential Diagrams

T. Uda, *Kyoto University*

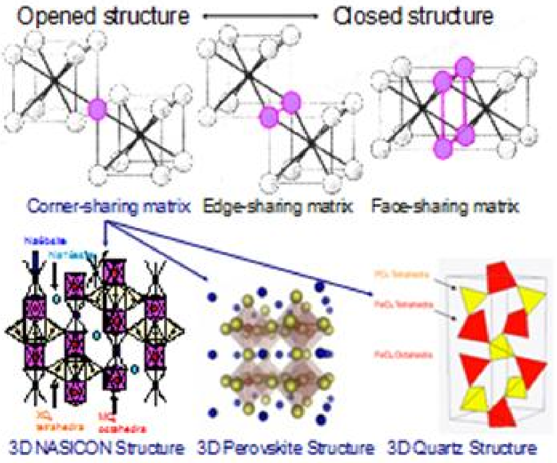
The development of new **phosphate electrolytes** for fuel cells, **phosphide semiconductors** for photovoltaic cells, and **calcium hydroxyapatite** for bio-materials by computational thermodynamics and the first principle calculations.



Development of Eco-friendly Post Lithium-ion Batteries

S. Okada, *Kyushu University*

Replacement of the rare-metal elements massively used in anode and cathode active materials of **lithium-ion battery** with economically and ecologically friendly elements such as sodium and iron.



Organic Molecular Approach to High-performance Rechargeable Batteries and Mechanistic Elucidation of Charge-discharge Processes

Y. Morita, *Osaka University*

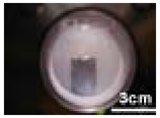
Organic molecule high performance rechargeable batteries by using the with multi-stage redox ability.

Electron structure Engineering (= atoms re-arrangement)

Considering function units not as the kind of elements
but its arrangement and consequently generated electron status.

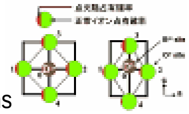
Design as lattice's structure
In sub-nano size order

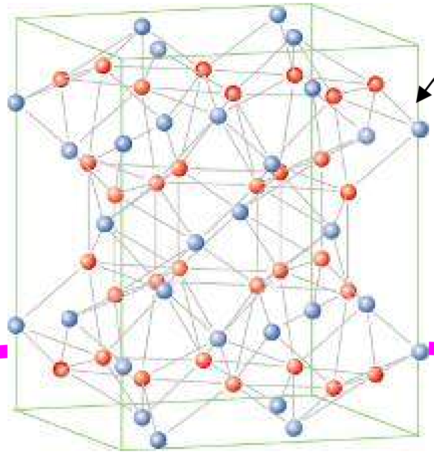
doping

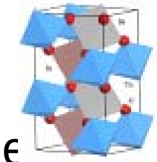


プラズマ水素ドーピング
by Ishigaki, nims

defect
圧電素子
by Ren, nims



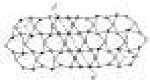


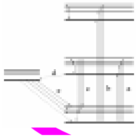


Atom alignme...
光触媒設計
by Ye, nims

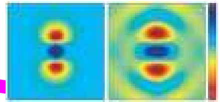
Artificial lattice

lattice
irregularit



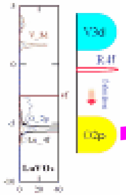


excitation

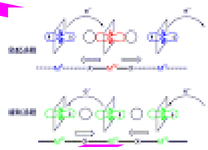


orbital

spin



Band gap



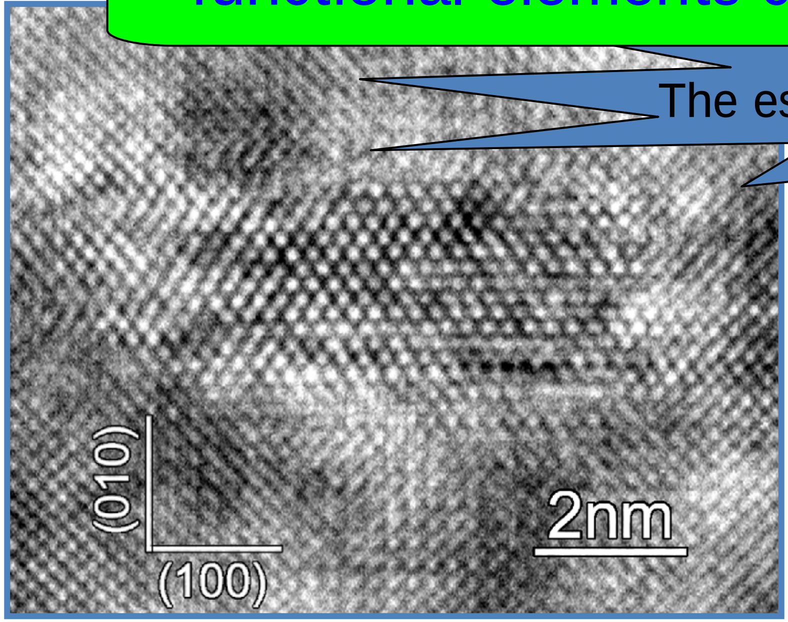
Lattice vibration

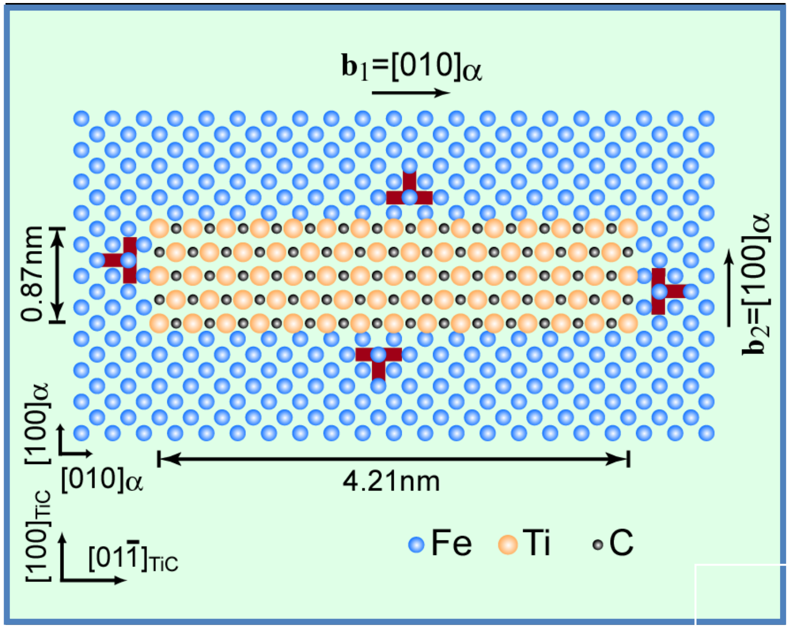
dielectri
piezoelectric
Young modulus
magnetic
Thermal expansion
thermoelectric
density
luminescence
conductivity
Emission
excitation
photonic
Thermal conductivit

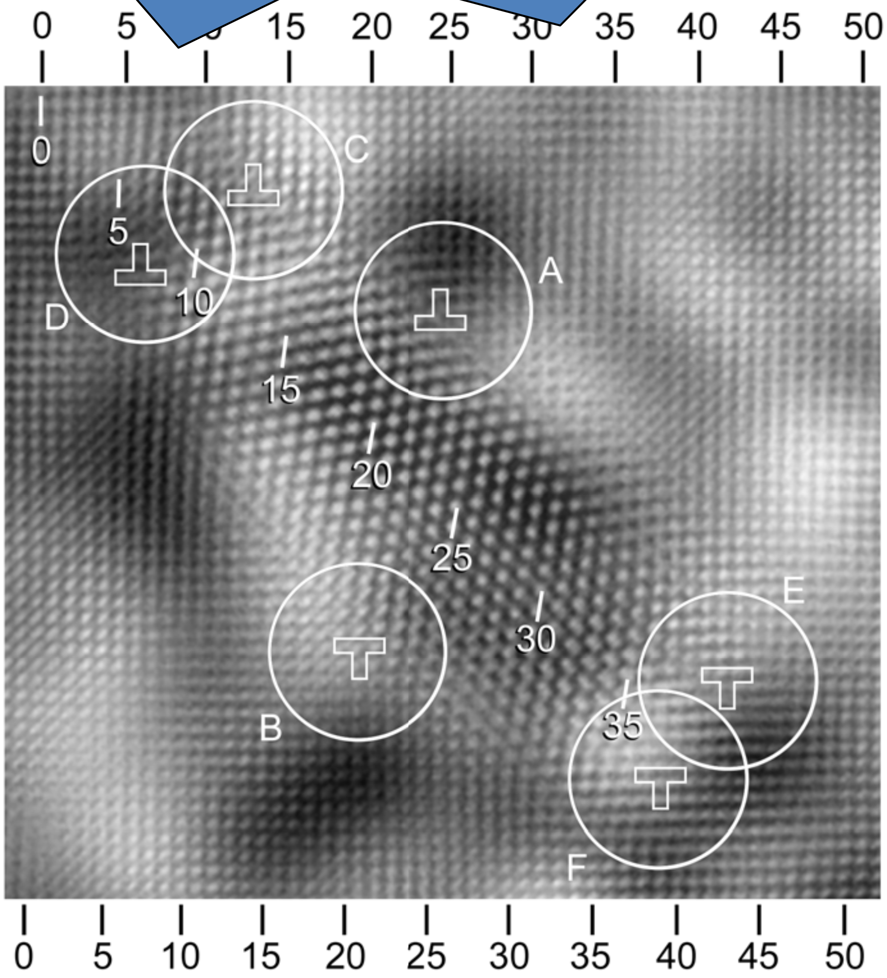
to enrich of the Possibility of Element Selection from common resources, Fe,Si,Al,Ca

functional elements can be observed in nano order

The essential is not composition but nano structure.

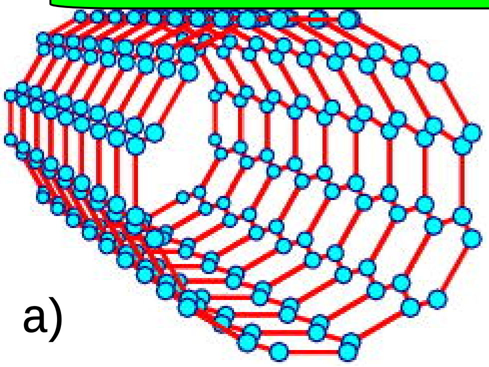




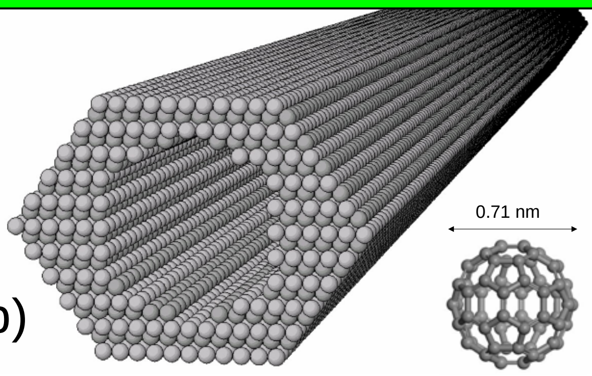


TiC nano-carbide in steel

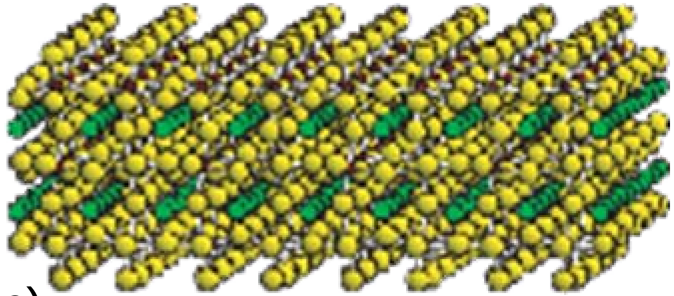
Nano fabrication realizes specially arranged structure



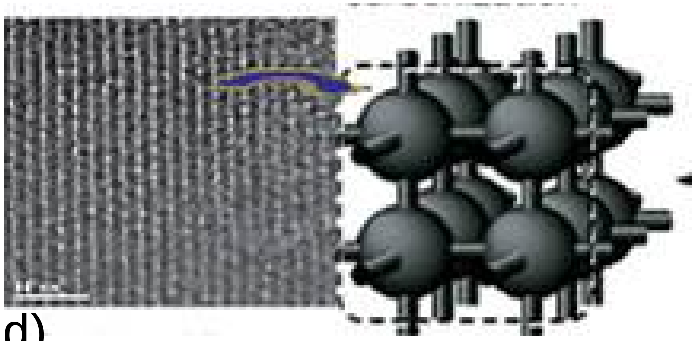
a)



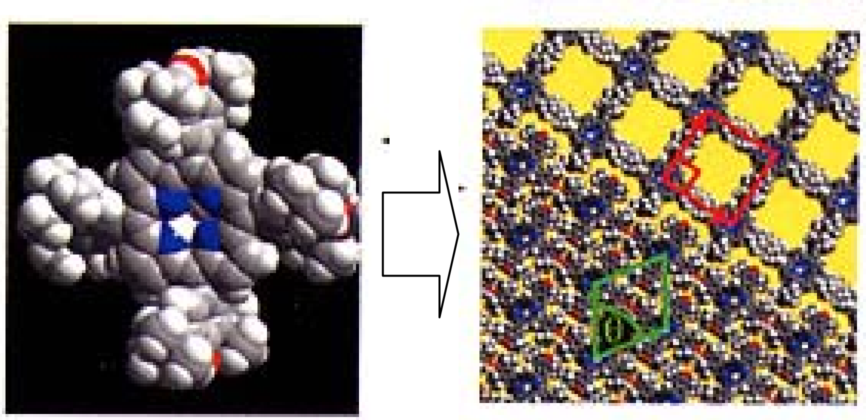
b)



c)



d)



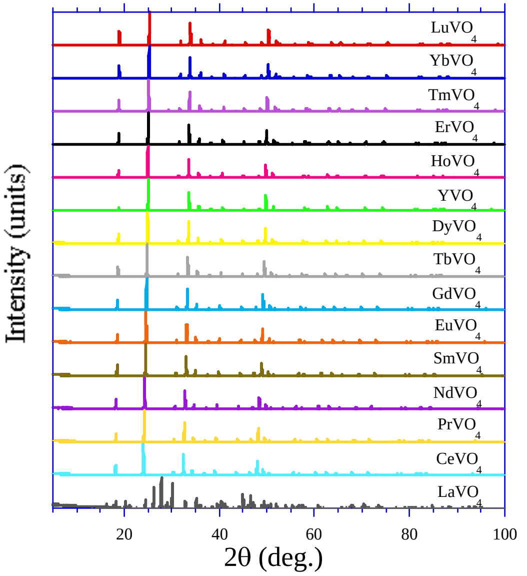
e)

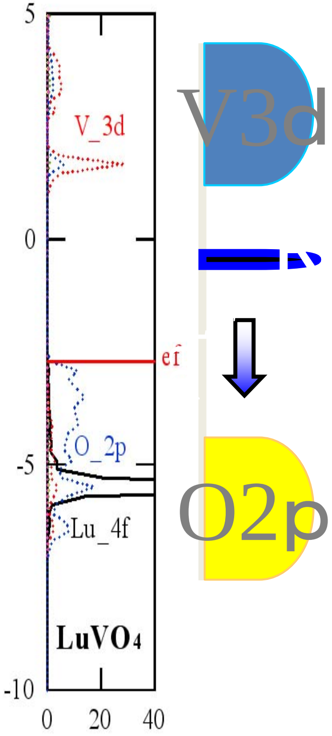
a) CNT
b) Fullerene nano wisker
c) Oxide nanosheet
d) Carbon nano cage
e) Molecular assembling

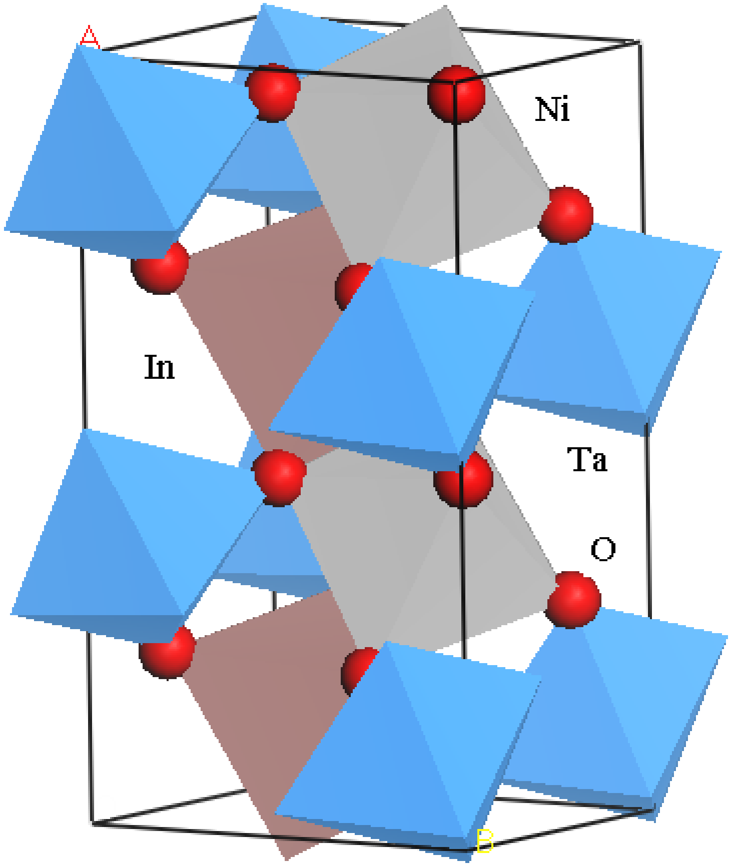
computer material design is powerful to explore material

Atomic arrangement calculation
in the field of photo-catalyst

Various photocatalysts are developed by band-gap design



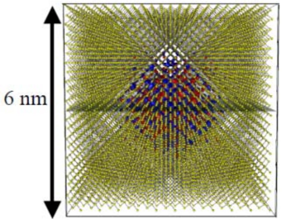




CeVO4, SmVO4, YVO4

First-principles simulations on reaction mechanism in energy-conversion materials

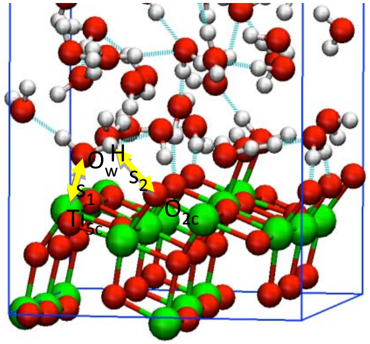
- Development of first-principles MD simulation codes
- Elucidation of reaction mechanisms by large-scale simulations



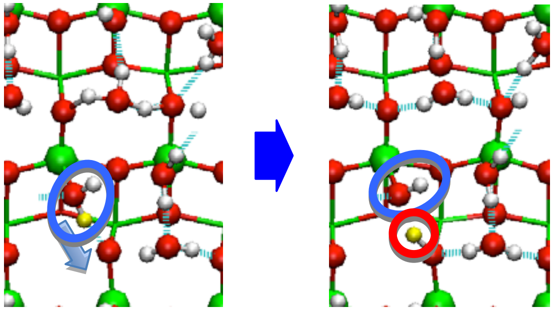
Large-scale simulations
for 10,000-atom systems

Water dissociation on photo-catalytic materials

TiO_2/H_2O interface

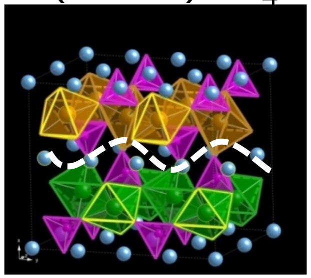


Reaction paths and barriers

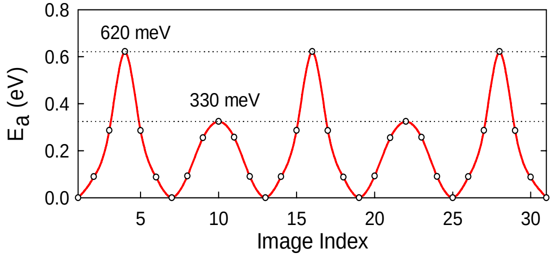


Li ion diffusion in Li battery materials

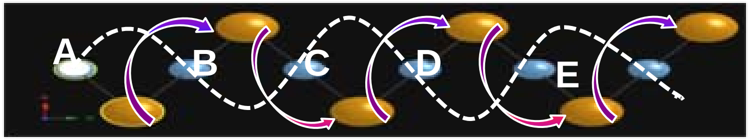
$Li(Fe,Mn)PO_4$



Li ion diffusion barrier



Diffusion path of Li associated with polaron hopping



Development of simulation tools
High-accurate large-scale simulations

Elucidation of mechanisms
underlying phenomenon

Determination of key factors
which control the reactions

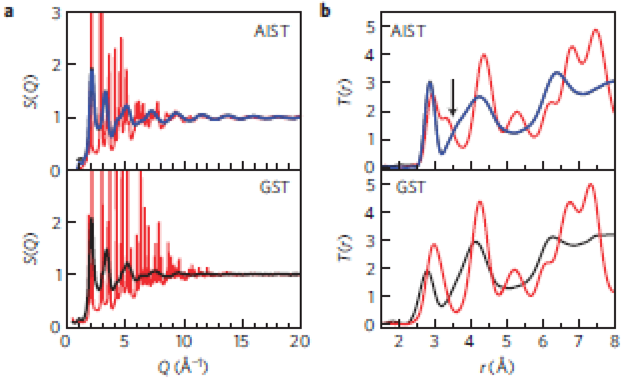
Optimization of key factors
High-throughput screening

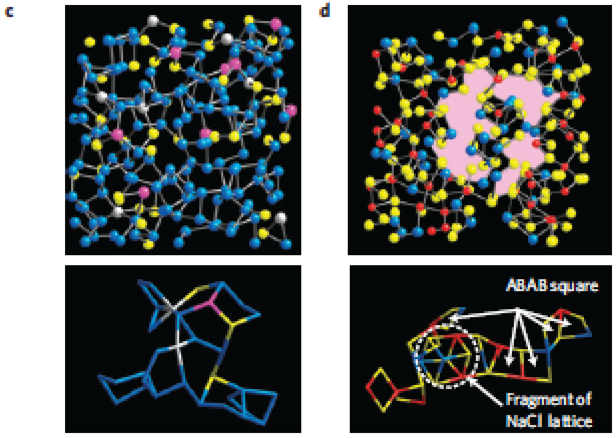
Element strategy

Materials design
High-efficient energy conversion

XRD, HAXPES and DFT-MD simulation of amorphous $Ge_2Sb_2Te_3$ and AgInSbTe and their phase change mechanisms

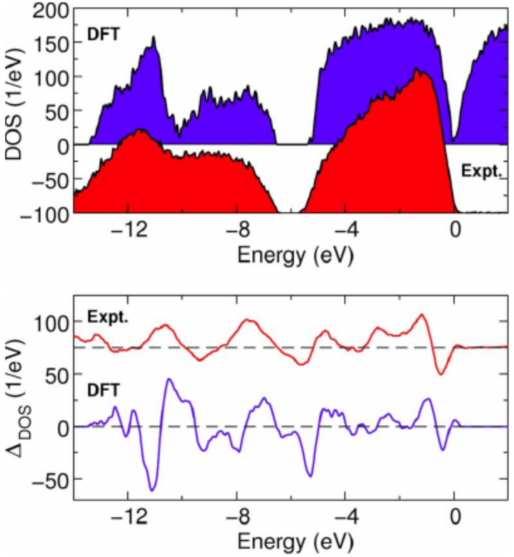
XRD of A and C phase AIST

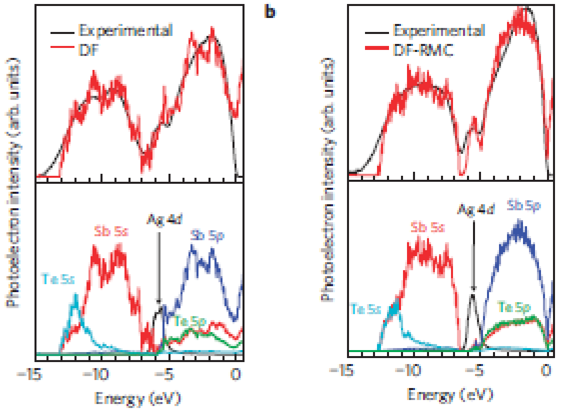




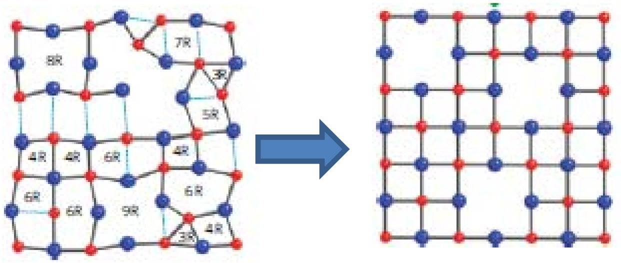
DFT-MD simulated A-structures in AIST(left) and GST(right).

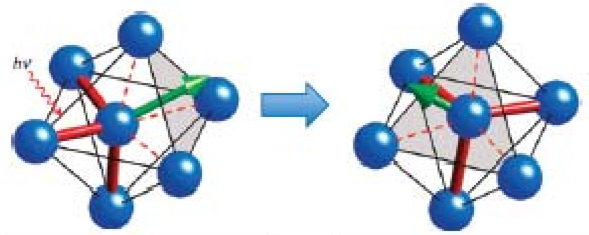
experimental and calculated valence band DOS of GST (upper and AIST(bottom).

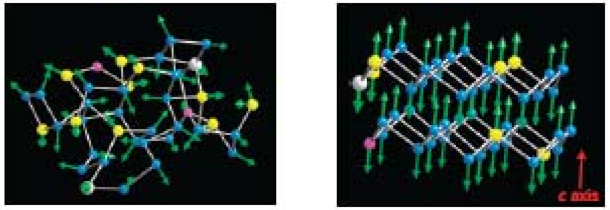




Phase change mechanism of GST (upper9 and AIST (bottom)



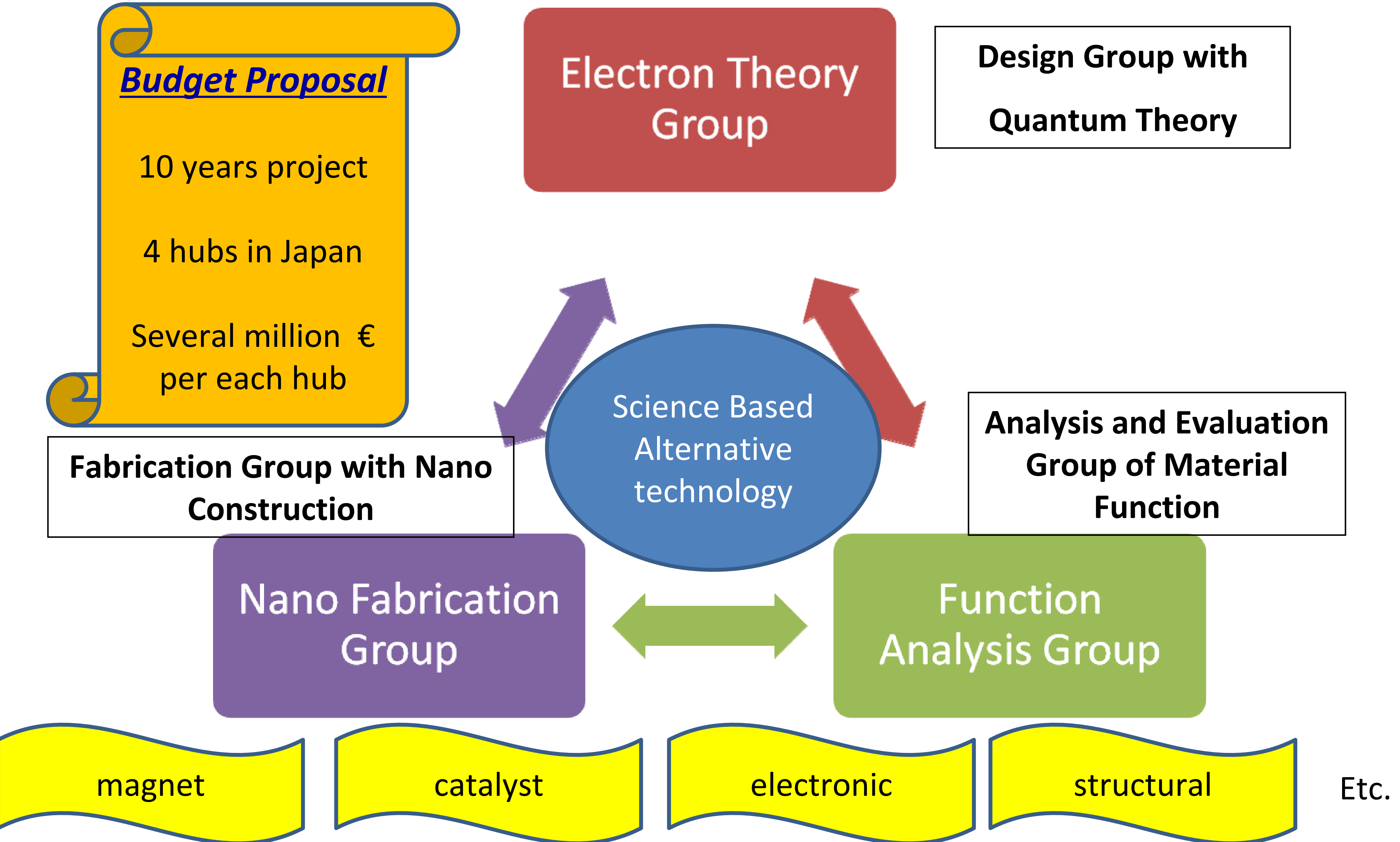




Large scale DFT-MD simulation combined with Reverse Monte Carlo analysis of XRD and valence bans density of states obtained by Hard X-ray photoelectron spectroscopy gives a clear cut picture of fast reversible crystalline-amorphous phase change mechanism. (Exp done at SPring-8.)

T. Matsunaga et al., NATURE MATERIALS VOL 10 , 129-134 (2011)

Next generation
Science and Technology on Elements Project



Budget Proposal

10 years project

4 hubs in Japan

Several million € per each hub

Electron Theory Group

Design Group with Quantum Theory

Science Based Alternative technology

Fabrication Group with Nano Construction

Nano Fabrication Group

Analysis and Evaluation Group of Material Function

Function Analysis Group

magnet

catalyst

electronic

structural

Etc.

What is the ultimate solution of the sustainable use of energy and resources?

For energy,

Utilization of solar energy from the Father Sun

For resources,

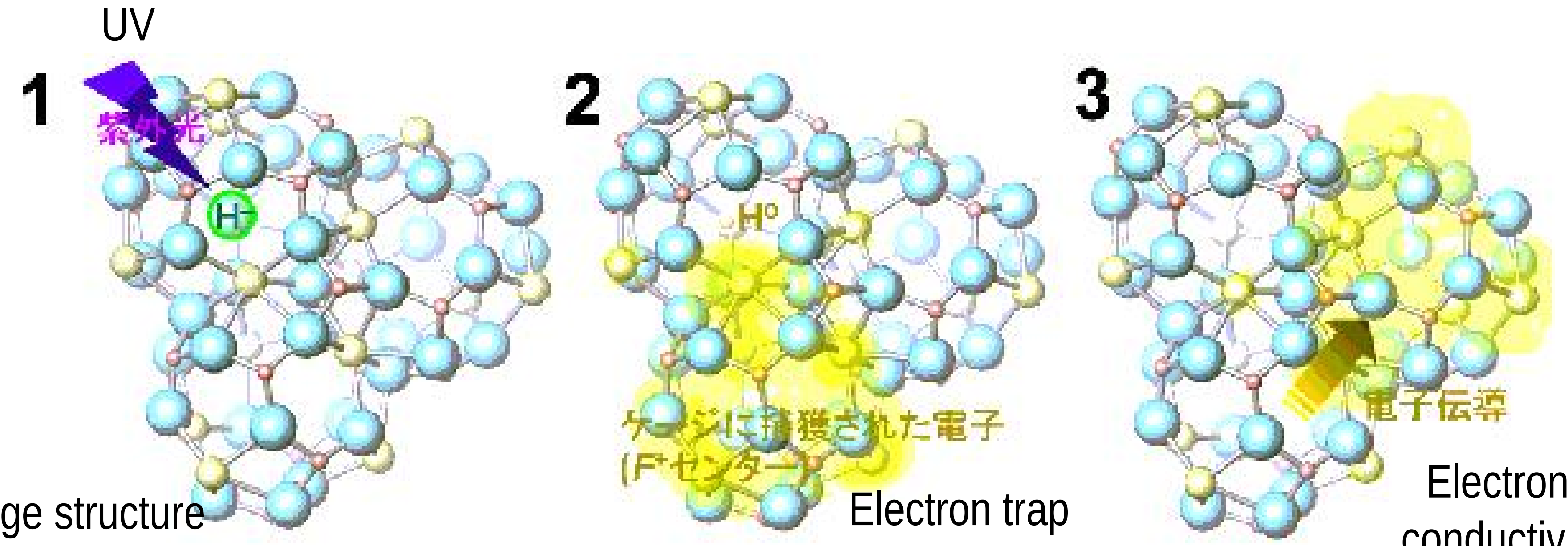
Utilization of soil composition (Si, Fe, Al, Ca, O etc.)
from the Mother Earth
and C as their children

Toward the solution, we endeavor to realize it.

Before the solution, we manage to supply the demand
by available technology.

Approach of Substitution

$12CaO \cdot 7Al_2O_3$ → optically transparent & electrically conductive



cage structure

can includes H^- ion substituted from free **O^-** ion which balances Ca+ by thermo-atmospheric control..

Electron trap

In cage structure

Electron conductivity

-> transparent semiconductor

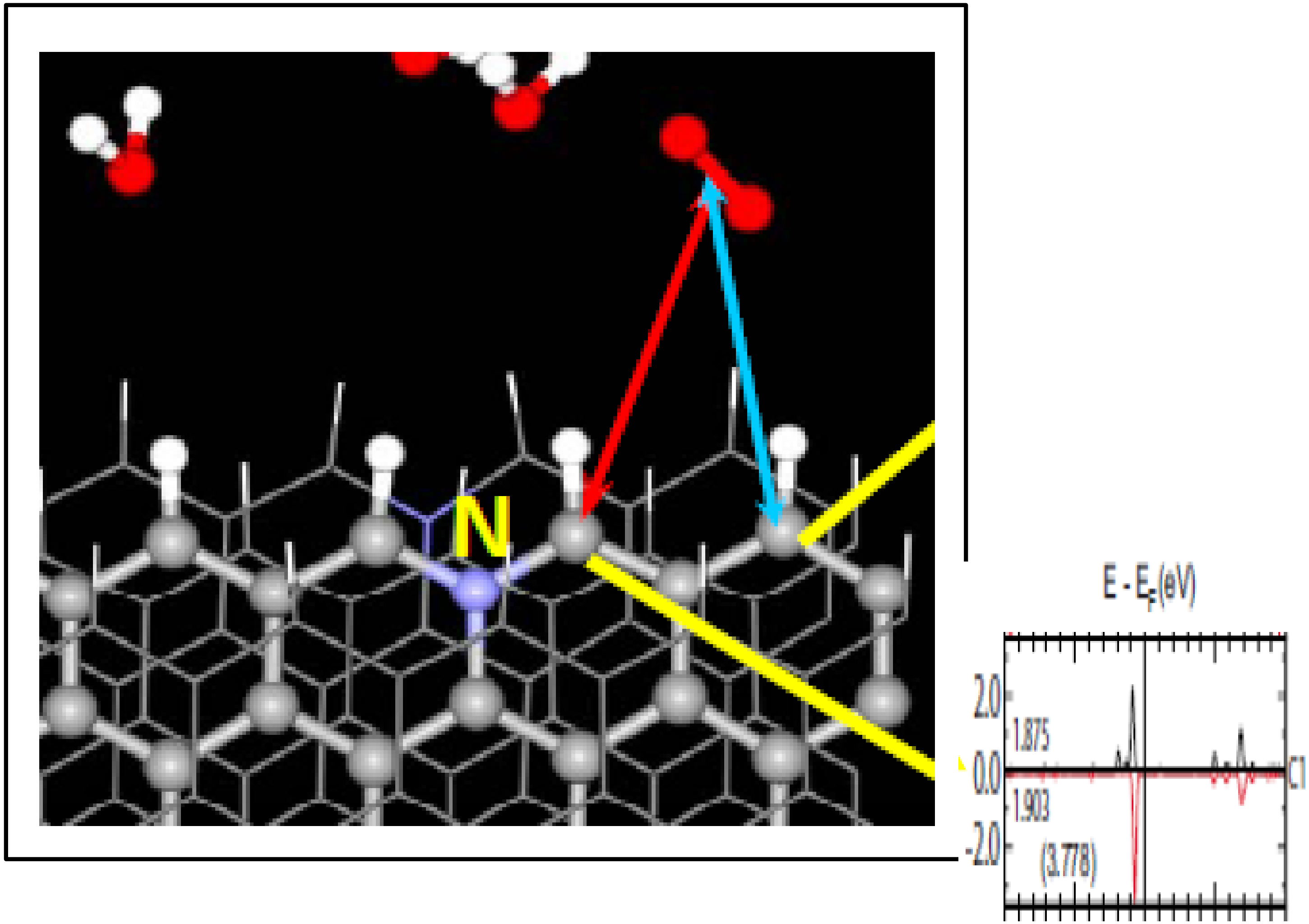
Cement material substitute Indium Tin Oxide

By Prof.Hosono, titech

Our known semiconductors are only a part of them.

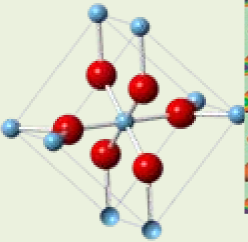
We have various kinds of unexplored semiconductor in our own backyard.

Carbon technology substitutes PGM used as catalyst
Nitrogen doped graphene makes similar electron structure with Pt catalyst

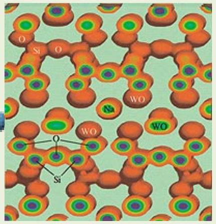


Carbon bonded to nitrogen

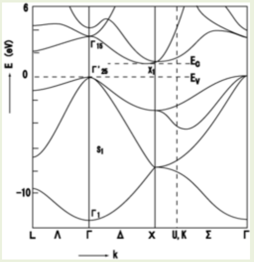
calculated electron structure database



Atomic structure



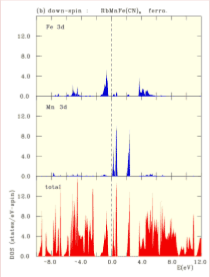
electron density distribution (real space)



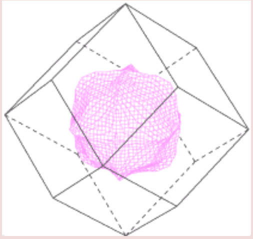
wave number -energy diagram

$\epsilon_{n\boldsymbol{k}}$

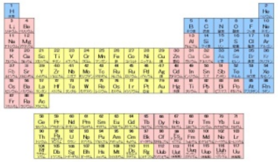
binary, ternary calculation and visualization



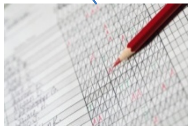
Electron density distribution (energy profile)



Fermi surface (energy profile)



binary、psedobinary
Covering calculation



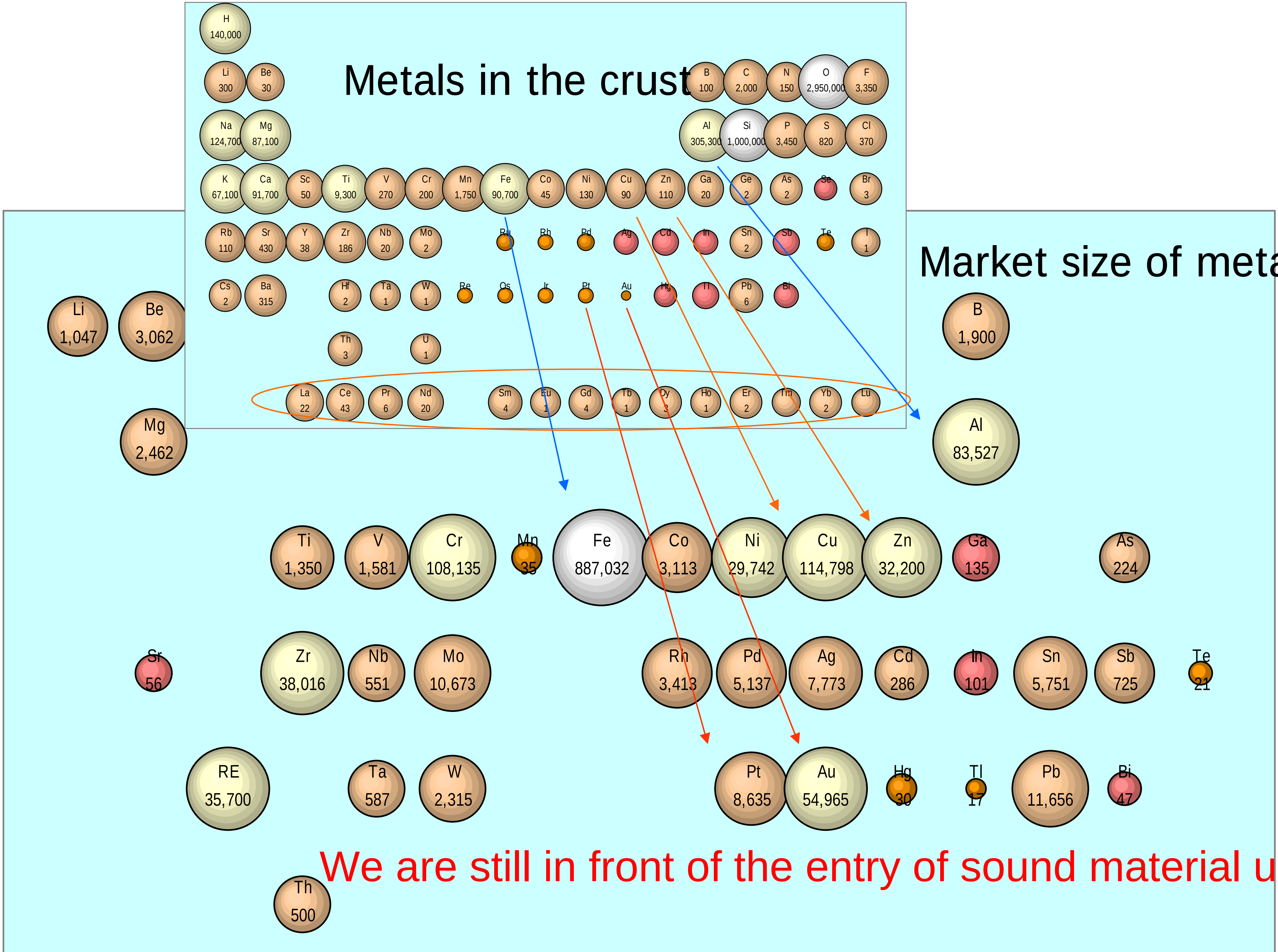
Common format

CompES (NIMS)

Electronic Structures Database(single、binary)
Crystal Structures Database
Element Properties Database

researcher

researcher



Metals in the crust

Market size of meta

We are still in front of the entry of sound material u

Thank you !!