Functional Materials Containing Arsenic and Other Hazardous Elements
— Development and practical use of new materials containing hazardous elements for sustainable society —

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Principles of action in 21st century

Safe, Environmentally conscious

Free from hazardous elements in materials

- Restricted use hazardous elements
  - **RoHS (EU)**  Cd <100 ppm, Pb <1000 ppm, Hg <1000 ppm
  - **REACH (EU)**  Arsenic compounds (As$_2$O$_3$, As$_2$O$_5$, etc.) <1000 ppm
  - **JIG (JPN, EU, US)**  Cd <100 ppm, Pb, Hg, Be, As, Sb, Bi, Se <1000 ppm

  - **Pb-Sn solder**  →  Sn-Ag-Cu, Sn-Zn-Bi solder
  - **Ni-Cd battery**  →  Li$^+$-ion battery
  - **Fluorescent lamp (Hg)**  →  GaN LED
  - **As$_2$O$_3$ antifoaming agent**  →  Sb$_2$O$_3$
  - **CdTe Solar cell**  →  Cu(In,Ga)(S,Se)$_2$ Solar cell

- To develop materials consisting of C, N, O, Si, Fe, Zn, Cu, ⋅⋅⋅ is encouraged
  - *ex)* In Japan, MEXT launched its Element Strategy Initiative in 2007

Amount of hazardous elements consumed has been decreasing
Production of non-ferrous metals

- **Copper production**
  - Concentration
  - Copper Ore → Copper concentrate
    - 20-30wt% Cu
    - CuFeS$_2$ (chalcopyrite), Cu$_3$AsS$_4$ (enargite), ...
  - Smelting & refining
  - Copper concentrate → Electrolytic copper
    - 99.99wt% Cu

- **Zinc production**
  - Concentration
  - Zinc Ore → Zinc concentrate
    - ZnS: 75~92%
    - PbS: 1~5%
    - FeS and FeS$_2$: 7~14%
    - SiO$_2$: 0.2~4%
    - CdS: 0.1~0.4%
  - Smelting & refining
  - Zinc concentrate → Electrolytic zinc
    - 99.99wt% Zn

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Non-Ferrous Metal Industry

- Supplying safe and abundant elements
  - Cu, Zn, Sn, ···
- Manufacturing various hazardous byproducts
  - As, Cd, Pb, Hg, ···

To produce only non-hazardous elements is impossible!

Output of hazardous elements will increase due to degrading of ore
How will hazardous elements be handled?

**Present answer:** We do **NOT USE** hazardous elements. They should be **STOCKED** securely.

cf) Minamata Convention on Mercury

**a. Eliminate hazardous elements from concentrates during mineral dressing**
Hazardous elements will be **STOCKED** in “Mineral-Producing Countries”
“Smelter Countries” will be **KEPT CLEAN**

*Environmental pollution in “Mineral-Producing Countries”*

**b. Eliminate hazardous elements during smelting**
Hazardous elements will be **STOCKED** in “Smelter Countries”
“Mineral-Producing Countries” will be **KEPT CLEAN**

*Storage space and cost in “Smelter Countries”*

Either “Mineral-Producing Countries” OR “Smelter Countries” will be afflicted by hazardous elements.

To continue amicable relations between “Mineral-Producing Countries” and “Smelter Countries” is difficult.

We have to find another solution
Safe elements vs. hazardous elements

Safe element; C, N, O, Si, Fe, Zn, Cu
Light element

Hazardous element; Cd, Pb, Hg, As
Heavy element

ZnO: Wide energy band gap, localized electronic states (Low electron mobility)
CdTe: Narrow energy band gap, delocalized electronic states (High electron mobility)

Heavy elements have specific functions that cannot be realized by light elements.
Safe elements vs. hazardous elements

It is not expedient to remove all hazardous elements from functional materials

*We had better to use hazardous elements in functional materials*

**Question:** Can we allow to use hazardous elements in functional materials?

**Answer:** Probably **YES**

But, limited to the **materials that are highly required to realize sustainable society**

ex) Electricity Generation, Electricity Storage, CO₂ reduction ・・・

cf) Radioactive elements used in the Nuclear Power Plant

Uranium (U), Plutonium (Pu) ・・・

cf) RoHS directive in EU countries

Arsenic is NOT restricted! ・・・ GaAs

Cadmium in solar cells and displays are exception! ・・・ CdTe & CdSe

*We should develop and use functional materials consisting of hazardous elements*
Scheme to utilize hazardous elements — an example —

Functional Materials containing hazardous elements

• They cannot used in consumer products
• They have to be under strict control
• Their use might be acceptable in the application that realize sustainable society

*When we develop materials containing Cd, As, Pb, ... for*

**Solar panels for large-scale solar power station**

- Solar farm in Japan
- Solar farm in mineral-producing countries

- **Elimination** of hazardous elements from concentrates will not be required more.
- A part of hazardous elements exported will return to the mineral-producing countries as clean electricity generator.
- Hazardous elements imported will create clean electricity in Japan.

Hazardous elements will be stocked evenly in mineral-producing countries and JPN

*We will be able to continue amicable diplomatic relations.*
CdTe solar cell business  First Solar, Inc.  (US)  http://www.firstsolar.com/
Promising materials

Gallium arsenide (GaAs)

Application I: Thin-film solar cell

![Graph showing efficiency trends from 1970 to 2020 for GaAs solar cells.]

- **28.9%** Alta Devices (US)
  - Highest efficiency in single-junction PV
  - *cf* CdTe: 22.1%
  - Cu(In,Ga)Se$_2$: 22.9%

Small Unmanned Systems,
High Altitude Long Endurance Aircraft, Space, Automotive

https://www.altadevices.com/
Promising materials

Indium arsenide (InAs)

Application I: Quantum Dot Solar Cells

Conversion Efficiency / %

<table>
<thead>
<tr>
<th>Band Gap / eV</th>
<th>0.5</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
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<tbody>
<tr>
<td>MEG: QD-PV</td>
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<tr>
<td>Bulk S.C.</td>
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<tr>
<td>InAs Quantum Dots</td>
<td>0.9 &lt; Eg &lt; 1.2eV</td>
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1 photon → 1 h-e pair
1 photon → >2 h-e pair

Safe synthesis method of InAs QDs using AsPh₃

Tri-phenyl arsine
AsPh₃

mp 60°C
bp 360°C
LC₅₀: 1/100~1/200 of As₂O₃
**Candidates**

**Cu₃AsS₄ (Enargite)**

Diamond-related Structure

![Cu₃AsS₄ structure diagram]

**Energy band gap**

Indirect = 1.19 eV  
Direct = 1.44 eV

**High conversion efficiency comparable with GaAs solar cell is expected!**
Cu$_3$AsS$_4$ (Enargite)


**Photovoltaic Applications**

*Conference Record of the IEEE Photovoltaic Specialists Conference*, 2774 (2016)

Photoelectrochemical performance

Enargite
Candidates

\[\text{Cd}_3\text{As}_2\]

- High electron mobility
- Fast response semiconductor

Infrared emitter
Summary

*Issues*

We have no experience of materials development, in which we actively use hazardous elements.

We do not know true potential of hazardous elements as components of functional materials.

We need financial support to develop new materials consisting of hazardous elements.