New functionalities in abundant element oxides: ubiquitous element strategy

Japan-EU Workshop “Substitution of Critical Raw Materials” @ EU Japan Office (Nov. 21)

nm-sized structure
μm-scale
m-sized structure

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Research on C12A7 led to a Science & Technology Policy

“Element Strategy for Sustainable society” National Policy (Started from 2008)

Ubiquitous Element Strategy

Function Structure Element

- size
- charge
- orbital
- spin
- theoretical
- defect
- measurement
- Unconventional Valence state

<table>
<thead>
<tr>
<th>Clark Number</th>
<th>Order</th>
<th>Element</th>
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<td>H</td>
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<tr>
<td>10</td>
<td>10</td>
<td>Ti</td>
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</table>
Electro-active materials made from 3 Structural Materials

Proposal of Transparent Amorphous Oxide Semiconductors (1995)

Fabrication of transparent flexible transistor (2004, Nature)

70-inches, UD, 240Hz LCD driven by TAOS-TFT Arrays (Samsung@ FPD Int ’10)

Focusing on Built-in nanostructure In 12CaO•7Al₂O₃ (1998)

Transparent metal from Cements

Conversion to Transparent metal. (2004, Science)

molten metallic electride (2011, Science)

Discovery of a new high Tc Supercond. since 1986

Highest Tc except Cuprates, “2nd fever” (2008, JACS & Nature)
SHARP has announced adoption of a-IGZO-TFTs for mobile LCDs (June 3, 2011)

亀山第2工場に「IGZO技術」を導入
Introduction of IGZO-TFT to Kameyama-2 factory

高精細・高画質・超低消費電力のモバイル液晶を生産
high precision, high quality
ultra low power assumption

仮想線「IGZO」を最先端ラインに導入
新素材IGZOを最先端ラインに導入

JST issued parent license (non-exclusive) of IGZO-TFT to Samsung EL

モバイル液晶の生産拡大
Production expansion of mobile LCD

tablet
computer
terminal

スマートフォン
ゲーム

車載用
アミューズメント

a-IGZO TFTs are going to apply to iPad3 with high resolution.
12CaO·7Al₂O₃ (C12A7)

- A constituent of alumina cements
- Large band gap ~7 eV
- Cubic (a = 1.199 nm, I₄₃d)
- Unit cell: Ca₂₄Al₂₈O₆₆ = [Ca₂₄Al₂₈O₆₄]⁺⁴ + 2O²⁻

- Mp. 1415 °C
- 12 Cages: 6x10²¹ cm⁻³
- Free Oxygen Ions: 1x10²¹ cm⁻³
- Densely Packed Sub-nano-sized Cages
- Fast Oxygen Ion Conductor
Electronic Structure of C12A7

Evac
WF=2.4eV

Energy (eV)

Conduction Band (Framework)

Wave functions confined in cages

Cage Conduction Band

O$_{2p}$ (Free Oxygen)

Valence Band (Framework)

Cage Conduction Band

Cage conduction band

Fermi edge

Hard XPS

Electron-doping to C12A7

\[ \text{[Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} (2\text{O}^{2-}) + \text{Ti} \rightarrow \text{[Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} (4e^-) + \text{TiO}_x \]

(Max \(2.3 \times 10^{21}\) cm\(^{-3}\))

Metal – Insulator Transition

Metal composed of typical insulators, lime and alumina!

Metallic state

Semiconducting state

Insulating state

\( \sigma = \sim 10^{-10}\text{S cm}^{-1} \)

\( N_c = \sim 1 \times 10^{21}\text{ cm}^{-3} \)

1.5x10^3 Scm\(^{-1}\)@RT

Band Conduction

Hopping Conduction

Nano Lett. 2007

Polaron : electron localized by lattice distortion
Metal-Superconducting Transition in C12A7:e⁻ single crystals

First s-metal superconductor at P=1atm

JACS.(2007)
Work function of C12A7:e⁻

~ 2.4 eV

<table>
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<tr>
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<th>Work Function (eV)</th>
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<tr>
<td>Eu</td>
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<td>C12A7:e⁻</td>
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<tr>
<td>Rb</td>
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<tr>
<td>Cs</td>
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</tr>
</tbody>
</table>

O-LED
E-gun

Alkaline
Alkaline earth
Rare earth
Unique Properties of C12A7:e⁻ metal: small workfunction and chemical inertness

\[ WF = 2.4 \text{eV} \]

(cage conduction band)

C12A7 world

- C12A7:O⁻
- C12A7:O₂⁻
- C12A7:O₂⁻

Low work function but stable

- Strong oxidation power

Field e-emitter

- Unique band structure

Cathode for OLED

- Surface Melt&Glass

UV(e-beam)-induced Insulator-conductor conversion

- Unique band structure

Metallic state

- Insulating state

3x10¹⁹cm⁻³
2x10²¹cm⁻³
3x10¹⁹cm⁻³
2x10²¹cm⁻³

ReRAM

Melt&Glass

Surface

reagents for organic reaction
Activation of Inert chemical species at C12A7 electride surface

- High density of electron trapped cages $\sim 10^{13}/\text{cm}^2$
- Low work function $\sim 2.4 \text{ eV}$

Activation by electron transfer

Is it possible?
STM Observation on C12A7:e⁻ surfaces

Ex Situ I-V characteristics
Enlarged View

(100)  (110)  (111)

3x3 nm, +2.5 V, 0.05 nA

small-mounds

stripes & dots

0.2 ~ 0.3 nm $\rightarrow$ atomistic order

$\sim 0.4$ nm

$\sim 0.2$ nm

$2 \sim 7^\circ$

$\sim 4$ nm
Surface model for (100)

**Bulk truncated**

(100) plane of C12A7:e− unit cell

**Cage conserved**

Open mouths: Not observed by experiments

- Atom density
- Thermal stability
- Conductivity
- Cage conserved
STM Images vs. Cage conserved model

(100)  (110)  (111)

X: Ca
White: Defect
Black: Adatom

ACS Nano (2011)
Can we obtain solvated electron in high temperature oxide melt/glass?

Liquid ammonia

Solvated cation  Solvated electron

M-I transition

Sodium electrolyte
Natriumelektrid
A solution of sodium in liquid ammonia.
Eine Lösung von Natrium in flüssigem Ammoniak.
Molten state of C12A7 electride: metallic conduction

C12A7:O²⁻ Melt

Ionic conducting

Metallic conducting

C12A7:e⁻ Melt

Transparent

Strongly Colored

Concentration of Solvated electrons

\(~10^{21}\text{cm}^{-3}\)

The photo was taken through a color filter

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