Novel Advanced Transparent Conductive Oxide:

*From atoms to the systems*

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Tyndall National Institute, Cork, Ireland
Tyndall National Institute

- Based in Cork, at Lee Maltings
Tyndall National Institute

• Established in 2004
• Brings together researchers in:
  – Photonics
  – Microelectronics
  – Nanotechnology
  – Microsystems
• Originally from the National Microelectronics Research Centre (NMRC), University College Cork (UCC) and Cork Institute of Technology (CIT)
• >350 research engineers, scientists, students, interns & support staff
• Creates a critical mass of researchers in the field of ICT
John Tyndall, 1820 - 1893

• Born in Leighlinsbridge, Co.Carlow 1820
• Prof. of Natural Philosophy, Royal Institution 1853
• Succeeded Faraday as Director of the Royal Institution 1863
• Initiated the practical teaching of science in schools
• Developed spectroscopy
• Invented the light pipe
• Tyndall Scattering - explained why the sky is blue
• Tyndallisation - sterilisation process
• Studies of the atmosphere
  - First to explain the “greenhouse effect”
Mission Statement:

‘Tyndall will be a Centre of Excellence for research, development and graduate training in Information and Communications Technology, recognised internationally for the quality of its outputs in materials, devices, systems and people, and its creation of new opportunities for Ireland’s economic growth.’
Outline

• Introduction
  - FP6-IST-C STREP NATCO project methodology for the search of new TCOs
  - Basic requirements for p-type TCOs
• First Principle modelling of Cu$_2$O and SrCu$_2$O$_2$
  - Electronic band structure
  - Stability
  - p-type conduction mechanism
• Microstructural, vibrational and optical properties of bulk and thin films polycrystalline SrCu$_2$O$_2$
  - X-ray diffraction studies
  - Fourier Transform Infrared studies
  - Raman studies
  - Spectroscopic ellipsometry/UV-VIS-NIR spectrophotometry
• Conclusions
From Atoms To Systems: 
*Generating Value From Research*

- Reverse the current trend of “lucky discovery” in material science
- Discovery of material with predetermined properties than proceed to synthesis and characterisation
- Theoretical work should coordinated with experimental work
Framework 6 Specific Targeted Research Project “NATCO”

- **NATCO**: Novel and Advanced Transparent Conductive Oxides
- *FP6-IST-C Future and Emerging Technology*

- **NATCO** main objective:
  - development of novel TCOs with enhanced electrical properties and tuned transparency
  - we focus on fundamentals, synthesis, characterisation, applications of $SrCu_2O_2$
  - Still much work required on $SrCu_2O_2$ before it can be used as a TCO
  - NATCO approach - combined modelling and experiment
“NATCO” consortium:
-7 partners/5 EU countries
Current and future applications for TCOs

- Transparent electrodes in flat panel displays (ITO)
- Organic light-emitting diodes,
- Touch-screen panels,
- Electrochromic windows,
- Electromagnetic shielding,
- Solar cells,
- Transparent electronics
Transparent conductive oxides (TCOs) are remarkable materials: co-existence of optical transparency and of electrical conductivity

- n-type TCOs are well known: ITO
- p-type TCOS are less prevalent

- wide band gap, \( E_g > 3.1 \text{ eV} \)
- no interband transition less than 3.1eV

- the ability to degenerately dope the oxide host with carrier concentration in excess of \( 10^{18} \text{cm}^{-3} \)
- highly dispersed valence band

- First report on p-type TCOs thin films, \( \text{CuAlO}_2 \), H. Kawazoe et al (Nature 389, 939, 1997)
NATCO methodology for new TCOs

- Choice of prototype material: NATCO choice was Cu$_2$O

- First principles modeling is used for a better understanding of the mechanism behind the p-type TCO properties of the prototype material

- First principles studies of doping and alloying Cu$_2$O prototype to propose new p-type TCO candidates

- In depth studies of optical, microstructural and electrical properties of p-type TCO candidates, both as bulk and as thin films
Origin of band structure of Cu$_2$O

Atomic structure of stoichiometric Cu$_2$O with a (2x2x2) unit cell

Red = oxygen, pink = copper

Direct band gap at $\Gamma$ point for Cu$_2$O: 0.47 eV

Band structure for Cu$_2$O
Why Cu$_2$O has small band gap?

Atomic structure of stoichiometric Cu$_2$O with a (2x2x2) unit cell

Red = oxygen, pink = copper

Two interpenetrating Cu-O-Cu networks, but not bonded!
(one light coloured and the other dark coloured)

Cu-Cu interactions are 3-dimensional network

Why Cu$_2$O have small band gap?

- Remove 1 Cu$_2$O network, but keep stoichiometry

- Band gap increased to 1eV

- Disrupt Cu-Cu inter-network interaction increases the bandgap
- Motivation for studying alloys of Cu$_2$O, e.g. CuAlO$_2$, SrCu$_2$O$_2$

First Principles Modelling of $\text{MCu}_2\text{O}_2$

*M* is alkaline earth, Mg, Ca, Sr, Ba

Tetragonal structure of $\text{MCu}_2\text{O}_2$:

- $\text{Cu}_2\text{O}$: Cu-Cu interactions are 3-dimensional

- $\text{MCu}_2\text{O}_2$: Cu-Cu interactions are along 1-dimensional ribbons → this increases band gap over $\text{Cu}_2\text{O}$ (A. Kudo et al. *Appl. Phys. Lett.* 1998, 73, 222; **A. Buljan et al., P. *Chem. Mat.* 2001, 13, 338)
Why $\text{SrCu}_2\text{O}_2$?

First principles density functional theory (DFT, PBE exchange-correlation functional) in plane wave basis set (396 eV cut-off, 2x2x1 Monkhorst-Pack sampling grid) to optimise lattice constants of $\text{MCu}_2\text{O}_2$ series

- Structure
- Stability
- Band gap
- Effective hole masses

Computed lattice constants:

<table>
<thead>
<tr>
<th>$\text{MCu}_2\text{O}_2$</th>
<th>$a$ [Å]</th>
<th>$b$ [Å]</th>
<th>$c$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>5.112</td>
<td>5.112</td>
<td>8.838</td>
</tr>
<tr>
<td>Ca</td>
<td>5.253</td>
<td>5.253</td>
<td>9.577</td>
</tr>
<tr>
<td>Sr</td>
<td>5.447</td>
<td>5.447</td>
<td>9.871</td>
</tr>
<tr>
<td>Ba</td>
<td>5.768</td>
<td>5.768</td>
<td>10.335</td>
</tr>
</tbody>
</table>

$\text{MCu}_2\text{O}_2$ lattice constants scale with ionic radius of alkaline earth:

$\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$

This will increase Cu-Cu distances → reduce Cu-Cu interactions → increase band gap
Are the alloys stable against decomposition into constituent oxides? i.e.

$$\Delta E = E(M\text{Cu}_2\text{O}_2) - [E(\text{Cu}_2\text{O}) + E(\text{MO})]$$

- \(E(M\text{Cu}_2\text{O}_2)\)-total energy of the bulk alloy,
- \(-E(\text{Cu}_2\text{O})\) and \(E(\text{MO})\) total energy of bulk \(\text{Cu}_2\text{O}\) and the bulk alkaline earth oxide in the rock salt structure

**MCu\(_2\)O\(_2\) chemical stability**

<table>
<thead>
<tr>
<th>(\text{MCu}_2\text{O}_2)</th>
<th>(\Delta E) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>+14 eV</td>
</tr>
<tr>
<td>Ca</td>
<td>+0.7 eV</td>
</tr>
<tr>
<td>Sr</td>
<td>-0.8 eV</td>
</tr>
<tr>
<td>Ba</td>
<td>-1.0 eV</td>
</tr>
</tbody>
</table>

- \(\text{MgCu}_2\text{O}_2\) and \(\text{CaCu}_2\text{O}_2\) are unstable
- \(\text{SrCu}_2\text{O}_2\) and \(\text{BaCu}_2\text{O}_2\) are stable.

They have shown that of these alloys only, Sr- and Ba have a negative Gibbs Free energy change for the formation of the alloy (from Cu₂O and MO)

### Origin?

Two sets of M-O distances

<table>
<thead>
<tr>
<th>Alloy</th>
<th>M²⁺–O in MCu₂O₂ / Å</th>
<th>M²⁺–O in MO / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCu₂O₂</td>
<td>1.95, 2.57</td>
<td>2.10</td>
</tr>
<tr>
<td>CaCu₂O₂</td>
<td>2.27, 2.63</td>
<td>2.40</td>
</tr>
<tr>
<td>SrCu₂O₂</td>
<td>2.44, 2.72</td>
<td>2.58</td>
</tr>
<tr>
<td>BaCu₂O₂</td>
<td>2.70, 2.89</td>
<td>2.77</td>
</tr>
</tbody>
</table>

Cation coordination and M-O distances impact on stability:

Mg: 4 coordinate in alloy
Ba: 6 coordinate in alloy

Mg-O distances deviate from Mg-O distances in MgO
Ba-O distances similar to Ba-O distances in BaO

Pink: Copper
Red: Oxygen
Green: Alkaline Earth
MCu$_2$O$_2$ Band Structure and Effective hole masses

MgCu$_2$O$_2$ (0.98 eV)

CaCu$_2$O$_2$ (1.47 eV)

SrCu$_2$O$_2$ (1.82 eV)

BaCu$_2$O$_2$ (1.57 eV)

m* = -0.41, -0.13, -7.47 $m_e$

m* = -0.44, -0.44, -2.26 $m_e$

m* = -9.60, -0.70, -1.90 $m_e$

Increasing band energy

X. Nie et al., PRB, 2002, 65, 075111 ,2002
Origin of p-type conductivity?

In Cu$_2$O: Cu vacancy formation is the origin of its p-type character

*Acceptor defect dominate over donor defects*


Formation energy of Cu vacancy (3 % concentration) = 0.41 eV

Formation energy of O vacancy (3 % concentration = 3.08 eV

Formation energy of Cu vacancy (3 %) = 0.57 eV

Formation energy of oxygen vacancy (3 %) = 3.86 eV

This model is generic (also holds for CuAlO$_2$,


With Cu vacancy in SrCu$_2$O$_2$: Band gap $\uparrow$ 1.88 eV

$m^* = -6.66, -0.91, -1.48$
In Cu$_2$O: Cu vacancy formation is the origin of its p-type character

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Formation energy of Cu vacancy (3 % concentration) = 0.41 eV

Formation energy of O vacancy (3 % concentration) = 3.08 eV


For SrCu$_2$O$_2$?

Formation energy of Cu vacancy (3 %) = 0.57 eV

Formation energy of oxygen vacancy (3 %) = 3.86 eV

*This model appears to be general for copper oxides*

(also holds for CuAlO$_2$, *M. Nolan, Thin Solid Films, 2008, 516, 8130)

With Cu vacancy in SrCu$_2$O$_2$: Band gap $\uparrow$1.88 eV

$m^* = -6.66, -0.91, -1.48$
Microstructural properties of bulk SrCu$_2$O$_2$

Good agreement between measured and calculated lattice parameters

\[
(a = b = 5.447 \text{\AA}, c = 9.871 \text{\AA})
\]

*X-ray diffraction profile from polycrystalline bulk SrCu$_2$O$_2$. The ticks correspond to the theoretical peak positions and peak intensities of the crystalline phases from the JCPS-ASTM databases listed on the upper figure.*
Optical properties of SrCu$_2$O$_2$

• Scarce information available and no report on optical constants so far

• Optical band gap reports:
  • SrCu$_2$O$_2$ and K doped SrCu$_2$O$_2$ thin films by PLD: $E_g=3.30$ eV obtained by direct inversion of $T$ and $R$ data* (A. Kudo et al, APL, 73, 220, 1998)

  • Bulk polycrystalline K doped SrCu$_2$O$_2$: $E_g=3.00$ eV, PES and IPES spectroscopy** (H. Ohta, J. Appl. Phys., 91, 5, 3074, 2002)

  • Bulk polycrystalline SrCu$_2$O$_2$: $E_g=3.35$ eV, spectroscopic ellipsometry (This work)
SrCu$_2$O$_2$ optical constants

PLD deposition on Si substrates, $T_{\text{dep}}=300^\circ\text{C}$,
Tetragonal SrCu$_2$O$_2$ Infrared active modes: bulk

Infrared active modes assigned for tetragonal SrCu$_2$O$_2$: 123, 166, 221, 289 and 579 cm$^{-1}$

**Mid-IR absorbance spectra of polycrystalline SrCu$_2$O$_2$ powder measured by ATR technique. Spectral resolution 4 cm$^{-1}$, 256 scans co-added. A**

**Far-IR DRIFT spectra of SrCu$_2$O$_2$ powder (supplied by Umicore). Spectral resolution 8cm$^{-1}$, 100 scans co-added.**

*Five infrared active modes assigned for tetragonal SrCu$_2$O$_2*
t-SrCu$_2$O$_2$ thin films: Infrared fingerprints

t-SrCu$_2$O$_2$ fingerprint at 575 cm$^{-1}$ (579 cm$^{-1}$ in the bulk)
Tetragonal SrCu$_2$O$_2$ Raman active modes: bulk

Four Raman active modes assigned for t-SrCu$_2$O$_2$: 183, 231, 284, 530 cm$^{-1}$
t-SrCu$_2$O$_2$ thin film: Raman characterisation

Raman highly sensitive to SrCu$_2$O$_2$ films crystalline quality
Optical transparency of PLD SrCu$_2$O$_2$ films

High transparency in Vis-NIR spectral range

Optical transmission and reflectance spectra of PLD SrCu$_2$O$_2$ thin films (200 nm thick, $T_{dep}$=300$^\circ$C)

Low surface roughness: 3nm

Fundamental absorption edge: 3.30eV

Consistent with previous reports of Hosono group:
A. Kudo et al, APL, 73, 220, 1998
Conclusion

• Modeling for insights into stability, band gap, defect chemistry
• Infrared and Raman active modes assigned for t-SrCu$_2$O$_2$
• Raman highly to disorder into SrCu$_2$O$_2$ films crystallinity (better than XRD)
• First determination on optical constants
• Understanding the mechanism enhancing Cu vacancies generation will enable improvement in SCO electrical properties
Acknowledgments

- Michael Nolan, Simon D. Elliott¹,
- Guy Garry, Bernard Servet, Olivier Durand²,
- Ekaterina Chikoidze³,
- Guido Huyberechts⁴,
- Evie L. Papadopoulou, Elias Aperathitis⁴,
- Odette Chaix, Jean-Luc Deschanvres⁵

¹Tyndall National Institute, Ireland;
²Thales Research & Technology France, France;
³GEMaC, CNRS-Université de Versailles-Saint-Quentin, France;
⁴Umicore Group Research & Development, Belgium
⁵IESL FORTH, Crete, Greece;
⁶LMGP, CNRS-INP Grenoble, France