Information Society Technologies

Novel Advanced Transparent Conductive Oxide:

From atoms to the systems

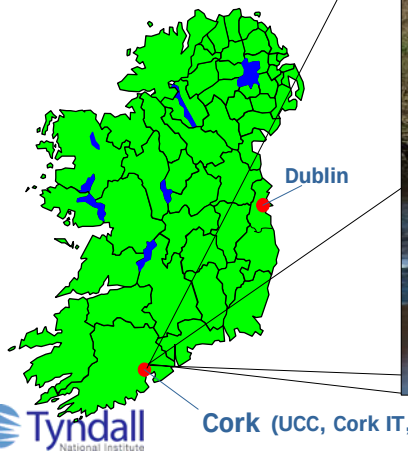
Mircea Modreanu

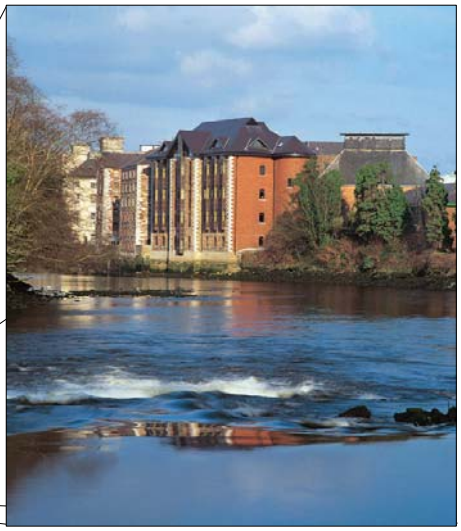
Tyndall National Institute, Cork, Ireland

Tyndall National Institute FORTH-IESL umicore THALES

Tyndall National Institute

- Based in Cork, at Lee Maltings





Tyndall National Institute

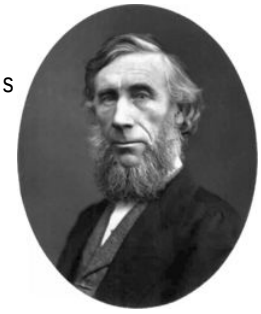
Tyndall National Institute

- 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

Tyndall National Institute

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"



Tyndall National Institute

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 .'

Tyndall National Institute

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_2O and $SrCu_2O_2$
  - *Electronic band structure*
  - *Stability*
  - *p-type conduction mechanism*
- Microstructural, vibrational and optical properties of bulk and thin films polycrystalline $SrCu_2O_2$
  - *X-ray diffraction studies*
  - *Fourier Transform Infrared studies*
  - *Raman studies*
  - *Spectroscopic ellipsometry/UV-VIS-NIR spectrophotometry*
- Conclusions

Tyndall National Institute

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

Tyndall National Institute

Framework 6 Specific Targeted Research Project "NATCO"

Information Society Technologies

- 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

Tyndall National Institute

"NATCO" consortium:

-7 partners/5 EU countries

Tyndall National Institute

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

Tyndall National Institute

Basic requirements for p-type TCOs

Transparent conductive oxides (TCOs) are remarkable materials: co-existence of optical transparency and of electrical conductivity

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

-wide band gap, E_g > 3.1 eV
-no interband transition less than 3.1eV
→ *Transparency*

-the ability to degenerately dope the oxide host with carrier concentration in excess of $10^{18}cm^{-3}$
-highly dispersed valence band
→ *Conductivity*

-First report on p-type TCOs thin films, *$CuAlO_2$*, H. Kawazoe et al (*Nature* 389, 939, 1997)

Tyndall National Institute

NATCO methodology for new TCOs

-Choice of prototype material: NATCO choice was Cu_2O

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

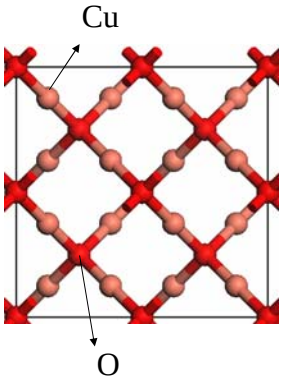
-First principles studies of doping and alloying Cu_2O prototype to propose new p-type TCO candidates

-In depth studies of optical, microstructural and electrical properties of p-type TCO candidates, both as bulk and as thin films

Tyndall National Institute

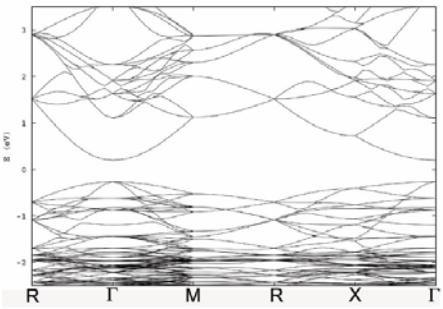
Origin of band structure of Cu_2O

Direct band gap at Γ point for Cu_2O: 0.47 eV



Atomic structure of stoichiometric Cu_2O with a (2x2x2) unit cell

Red = oxygen, pink = copper



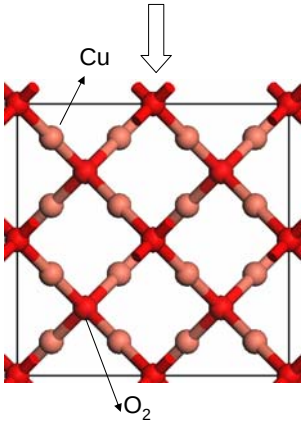
Band structure for Cu_2O

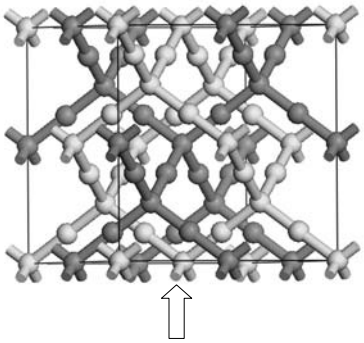
Tyndall National Institute

Why Cu_2O has small band gap?

Atomic structure of stoichiometric Cu_2O 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

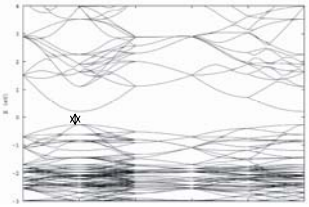
M. Angels Carvajal et al, Chem. Eur. J. 2004, 10, 2117,
A.Filippetti et al Phys. Rev. B 2005, 72, 035128,
H. Raebiger et al. Phys. Rev. B, 2007, 76, 045209
M. Nolan et al, Chem Mat, 2008, 20, 5522

Tyndall National Institute

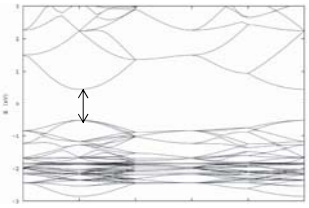
Why Cu_2O have small band gap?

- Remove 1 Cu_2O network, but keep stoichiometry

-Band gap increased to 1eV



Band structure for Cu_2O



Band structure for Cu_2O with one network removed.

-Disrupt Cu-Cu inter-network interaction increases the bandgap

-Motivation for studying alloys of Cu_2O, e.g. $CuAlO_2$, $SrCu_2O_2$

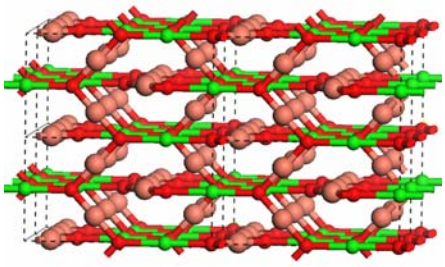
M. Nolan et al, Chem Mat, 2008, 20, 5522; H. Kawazoe et al *Nature* 389, 939, 1997, *A .Buljan, et al. Chem. Mater.* ***2001****, 13, 338*, X. Nie et al PRB, 65, 075111 ,2002)

Tyndall National Institute

First Principles Modelling of MCu_2O_2

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

Tetragonal structure of MCu_2O_2:



Pink: Copper

Red: Oxygen

Green: Alkaline Earth

-Cu_2O: Cu-Cu interactions are 3-dimensional

MCu_2O_2: Cu-Cu interactions are along 1-dimensional ribbons → this increases band gap over Cu_2O (A. Kudo et al. *Appl. Phys. Lett*. 1998, *73*, 222; **A. Buljan et al., P. *Chem. Mat*. 2001, *13*, 338)

Tyndall National Institute

Why $SrCu_2O_2$?

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 MCu_2O_2 series

-Structure

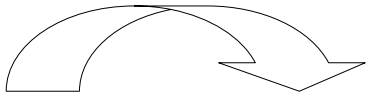
-Stability

-Band gap

-Effective hole masses

Computed lattice constants:

MCu_2O_2	a [Å]	b [Å]	c [Å]
Mg	5.112	5.112	8.838
Ca	5.253	5.253	9.577
Sr	5.447	5.447	9.871
Ba	5.768	5.768	10.335



MCu_2O_2 lattice constants scale with ionic radius of alkaline earth:

Mg < Ca < Sr < Ba

This will increase Cu-Cu distances → reduce Cu-Cu interactions → increase band gap

Tyndall National Institute

MCu_2O_2 chemical stability

Are the alloys stable against decomposition into constituent oxides? i.e.

$$\Delta E = E(MCu_2O_2) - [E(Cu_2O) + E(MO)]$$

-$E(MCu_2O_2)$-total energy of the bulk alloy,

-$E(Cu_2O)$ and E(MO) total energy of bulk Cu_2O and the bulk alkaline earth oxide in the rock salt structure

Computed ΔE

MCu_2O_2	ΔE [eV]
Mg	+14 eV
Ca	+0.7 eV
Sr	-0.8 eV
Ba	-1.0 eV

- **$MgCu_2O_2$ and $CaCu_2O_2$ are unstable**
- **$SrCu_2O_2$ and $BaCu_2O_2$ are stable.**

Tyndall National Institute

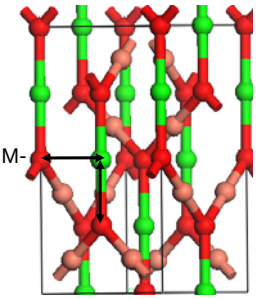
MCu_2O_2 chemical stability

R. Kucharski et al J.of Thermal Analysis and Calorimetry, 2000, 219/G. Moiseev et al. Thermochim. Acta, 1998, 318, 201/O. Vikhreva et al. Ceramics International, 1999, 25, 153 → have studied thermodynamic properties of MCu_2O_2

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 Cu_2O and MO)

Origin?



Two sets of M-O distances

Pink: Copper
Red: Oxygen
Green: Alkaline Earth

Compare M-O distances in alloy and rock salt MO oxide:

Alloy	M^{2+}–O in MCu_2O_2 / Å	M^{2+}–O in MO / Å
$MgCu_2O_2$	1.95, 2.57	2.10
$CaCu_2O_2$	2.27, 2.63	2.40
$SrCu_2O_2$	2.44, 2.72	2.58
$BaCu_2O_2$	2.70, 2.89	2.77

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

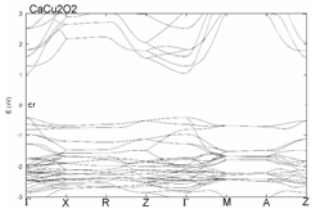
Ba-O distances similar to Ba-O distances in BaO

Tyndall National Institute

MCu_2O_2 Band Structure and Effective hole masses

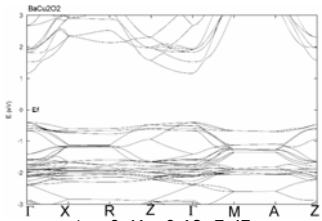
$MgCu_2O_2$ (0.98 eV)

$CaCu_2O_2$ (1.47 eV)



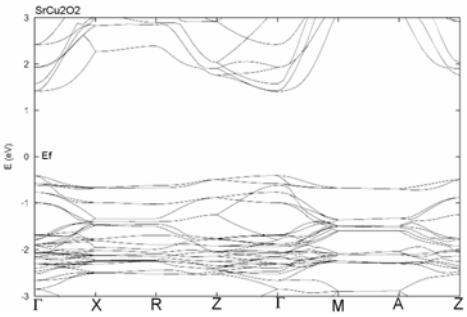
m* = -0.44, -0.44, -2.26 m_e

$BaCu_2O_2$ (1.57 eV)



m* = -0.41, -0.13 -7.47 m_e

$SrCu_2O_2$ (1.82 eV)



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

Increasing band energy

X. Nie et al., PRB, 2002, 65, 075111 ,2002

Tyndall National Institute

Origin of p-type conductivity?

In Cu_2O: Cu vacancy formation is the origin of its p-type character

Acceptor defect dominate over donor defects

*(*M. Nolan et al, Phys. Chem. Chem. Phys, 2006, 8, 5350; **H. Raebiger et al., Phys. Rev. B, 2007, 76, 045209)*

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

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

Tyndall National Institute

Origin of p-type conductivity?

In Cu_2O: 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

*(*M. Nolan et al, Phys. Chem. Chem. Phys, 2006, 8, 5350; **H. Raebiger et al., Phys. Rev. B, 2007, 76, 045209)*

For $SrCu_2O_2$?

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

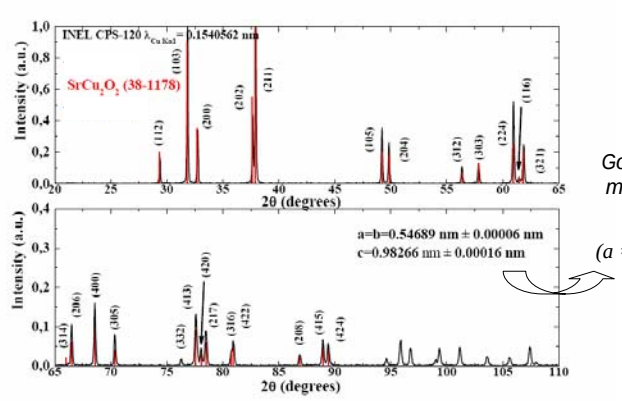
(also holds for $CuAlO_2$, **M. Nolan, Thin Solid Films, 2008, 516, 8130*)

With Cu vacancy in $SrCu_2O_2$: Band gap ↗1.88 eV

m* = -6.66, -0.91, -1.48

Tyndall National Institute

Microstructural properties of bulk $SrCu_2O_2$



Good agreement between measured and calculated lattice parameters

($a = b = 5.447Å$, $c = 9.871Å$)

X-ray diffraction profile from polycrystalline bulk $SrCu_2O_2$. 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

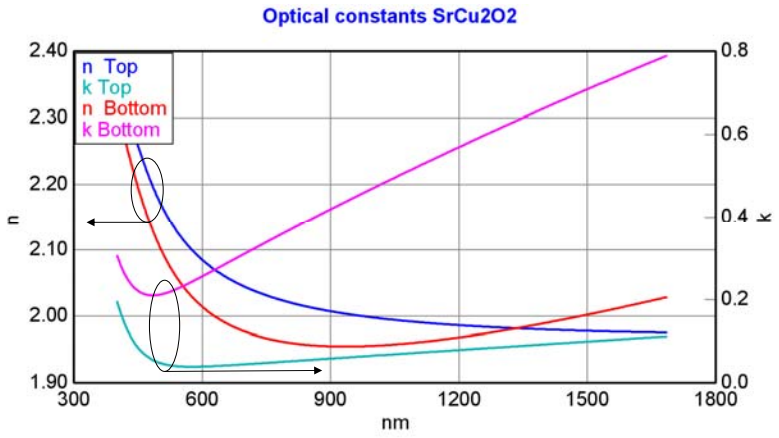
Tyndall National Institute

Optical properties of $SrCu_2O_2$

- Scarce information available and no report on optical constants so far
- Optical band gap reports:
  - $SrCu_2O_2$ and K doped $SrCu_2O_2$ 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 $SrCu_2O_2$: E_g=3.00 eV, PES and IPES spectroscopy**(**H.Ohta, J. Appl. Phys., 91, 5, 3074, 2002)*
  - Bulk polycrystalline $SrCu_2O_2$: Eg= 3.35 eV , spectroscopic ellipsometry *(This work)*

Tyndall National Institute

$SrCu_2O_2$ optical constants

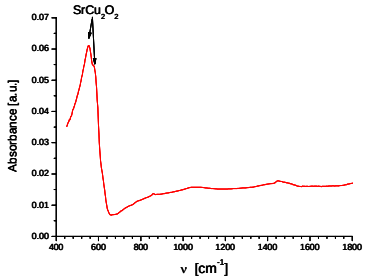


PLD deposition on Si substrates, T_{dep}=300°C,

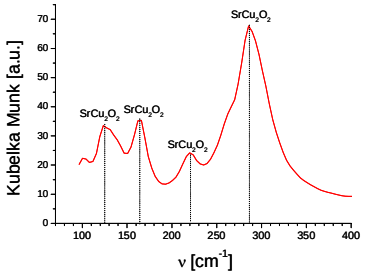
Tyndall National Institute

Tetragonal $SrCu_2O_2$ Infrared active modes: bulk

Infrared active modes assigned for tetragonal $SrCu_2O_2$:*123, 166, 221, 289 and 579 cm^{-1}*



Mid-IR absorbance spectra of polycrystalline $SrCu_2O_2$ powder measured by ATR technique. Spectral resolution 4 cm-1, 256 scans co-added. A

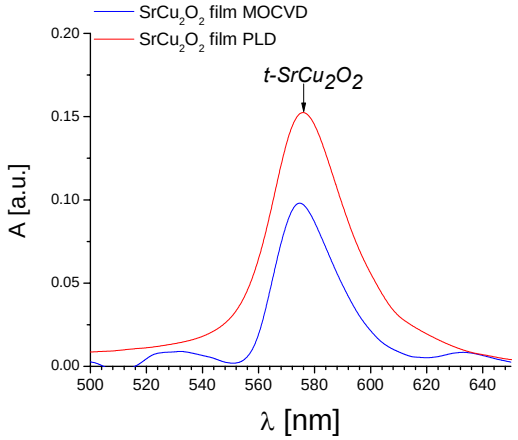


Far-IR DRIFT spectra of $SrCu_2O_2$ powder (supplied by Umicore). Spectral resolution 8cm^{-1}, 100 scans co-added.

Five infrared active modes assigned for tetragonal $SrCu_2O_2$

Tyndall National Institute

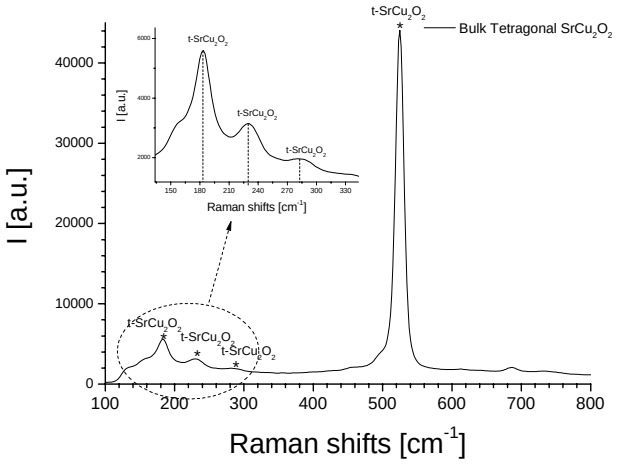
t-$SrCu_2O_2$ thin films: Infrared fingerprints



t-$SrCu_2O_2$ fingerprint at 575cm^{-1} (579cm^{-1} in the bulk)

Tyndall National Institute

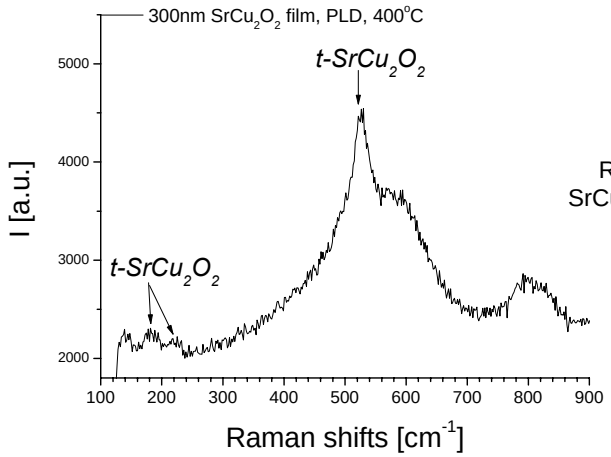
Tetragonal $SrCu_2O_2$ Raman active modes: bulk



Four Raman active modes assigned for t-$SrCu_2O_2$: 183, 231, 284, 530 cm^{-1}

Tyndall National Institute

t-$SrCu_2O_2$ thin film: Raman characterisation



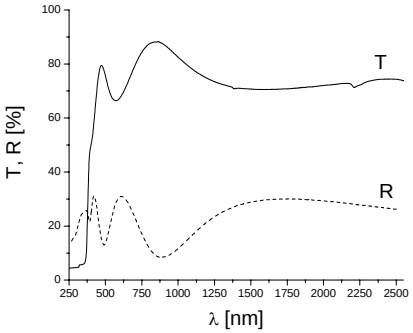
Raman highly sensitive to $SrCu_2O_2$ films crystalline quality

$SrCu_2O_2$ thin films, PLD, 400°C

Tyndall National Institute

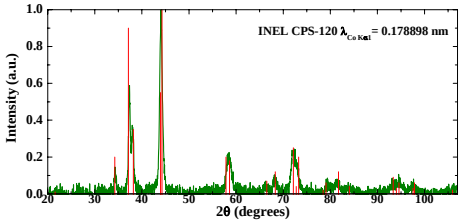
Optical transparency of PLD $SrCu_2O_2$ films

High transparency in Vis-NIR spectral range



Optical transmission and reflectance spectra of PLD $SrCu_2O_2$ thin films (200 nm thick, T_{dep}=300°C)

Low surface roughness: 3nm



XRD patterns for the PLD $SrCu_2O_2$ thin films (200nm thick) . The red lines show the position and the intensities for $SrCu_2O_2$ (JCPDS-ICDD: 38-1178)

Fundamental absorption edge: 3.30eV

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

Tyndall National Institute

Conclusion

- Modeling for insights into *stability, band gap, defect chemistry*
- Infrared and Raman active modes assigned for t-$SrCu_2O_2$
- Raman highly to disorder into $SrCu_2O_2$ films crystallinity *(better than XRD)*
- First determination on optical constants
- Understanding the mechanism enhancing Cu vacancies generation will enable improvement in SCO electrical properties

Tyndall National Institute

Acknowledgments

- Michael Nolan, Simon D.Elliott[1],
- Guy Garry, Bernard Servet, Olivier Durand[2],
- Ekaterina Chikoidze[3],
- Guido Huyberechts[4],
- Evie L. Papadopoulou, Elias Aperathitis[4],
- Odette Chaix, Jean-Luc Deschanvres[5]

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

Tyndall National Institute