



# Novel Advanced Transparent Conductive Oxide:

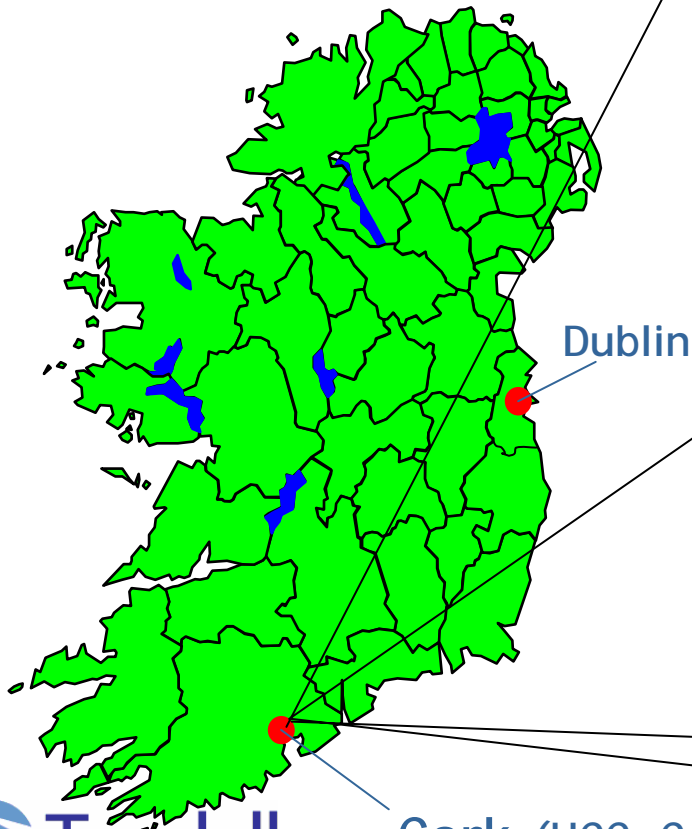
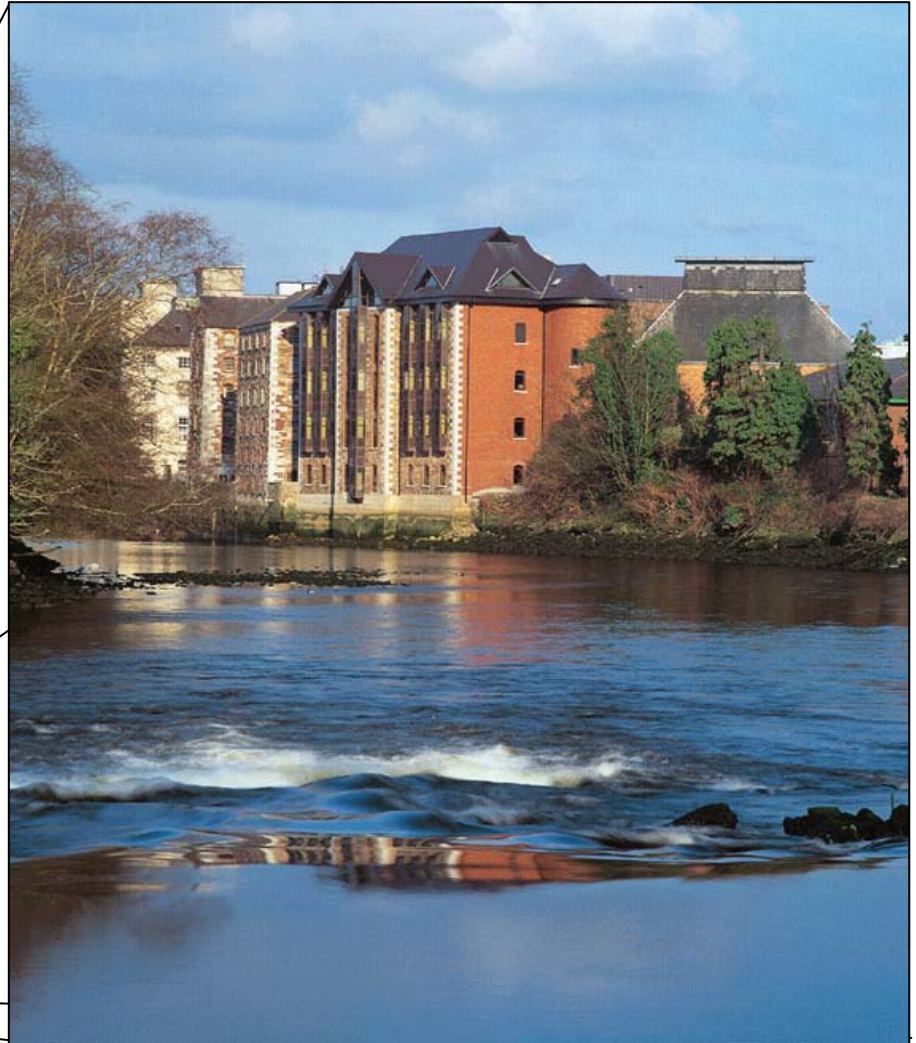
## *From atoms to the systems*

Mircea Modreanu

Tyndall National Institute, Cork, Ireland

# Tyndall National Institute

- Based in Cork, at Lee Maltings



Dublin

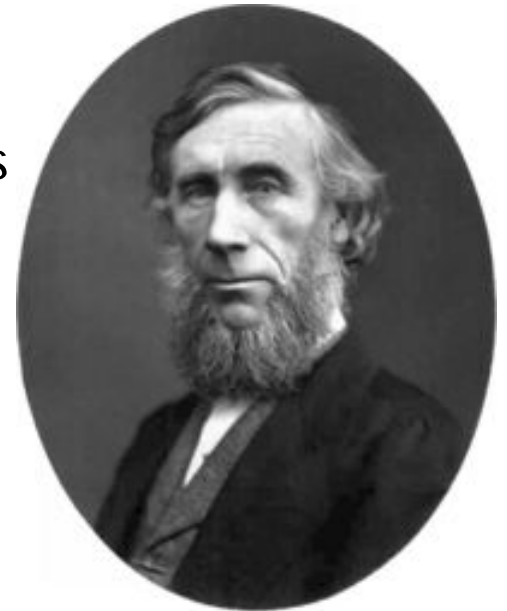
Cork (UCC, Cork IT, Tyndall)

# 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  $\text{Cu}_2\text{O}$  and  $\text{SrCu}_2\text{O}_2$ 
  - *Electronic band structure*
  - *Stability*
  - *p-type conduction mechanism*
- Microstructural, vibrational and optical properties of bulk and thin films polycrystalline  $\text{SrCu}_2\text{O}_2$ 
  - *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

# 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  $10^{18}\text{cm}^{-3}$   
-highly dispersed valence band

} → *Conductivity*

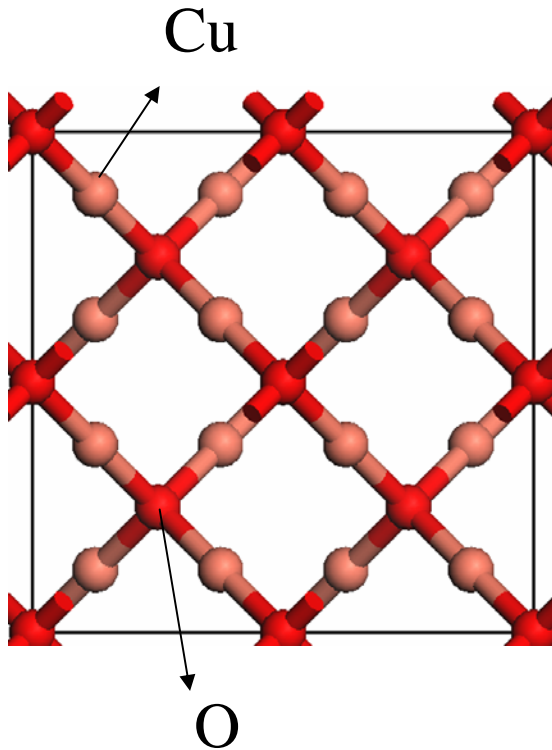
-First report on p-type TCOs thin films,  $\text{CuAlO}_2$ , H. Kawazoe et al (*Nature* 389, 939, 1997)

# NATCO methodology for new TCOs

- Choice of prototype material: NATCO choice was  $\text{Cu}_2\text{O}$
- 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  $\text{Cu}_2\text{O}$  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

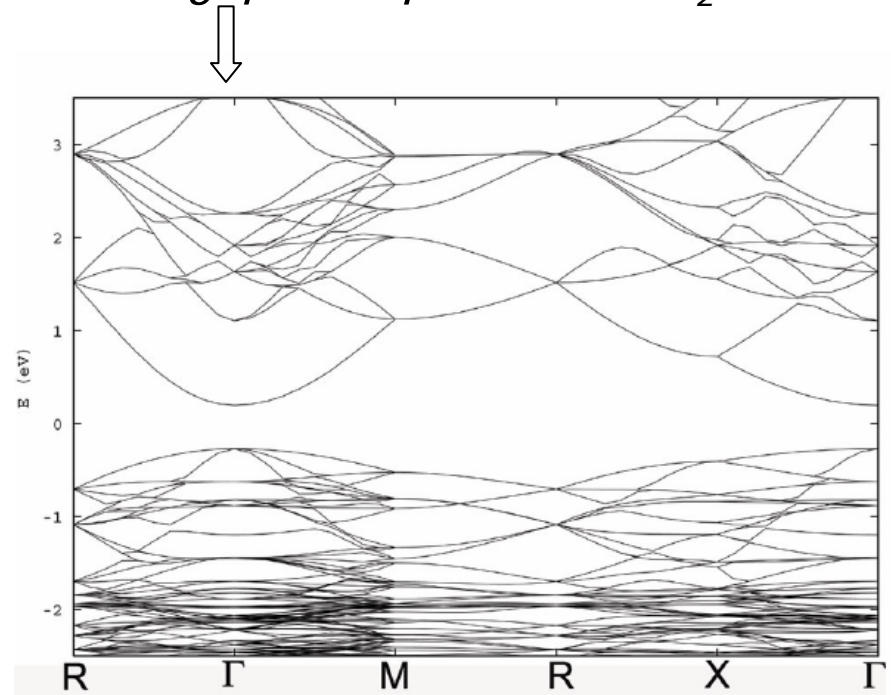
# Origin of band structure of $\text{Cu}_2\text{O}$

*Direct band gap at  $\Gamma$  point for  $\text{Cu}_2\text{O}$ : 0.47 eV*



Atomic structure of stoichiometric  $\text{Cu}_2\text{O}$  with a  $(2 \times 2 \times 2)$  unit cell

*Red = oxygen, pink = copper*

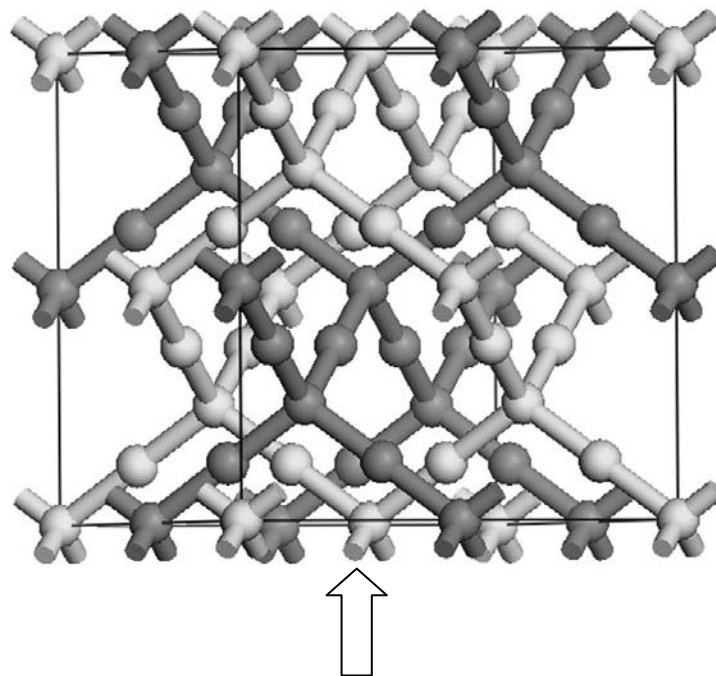
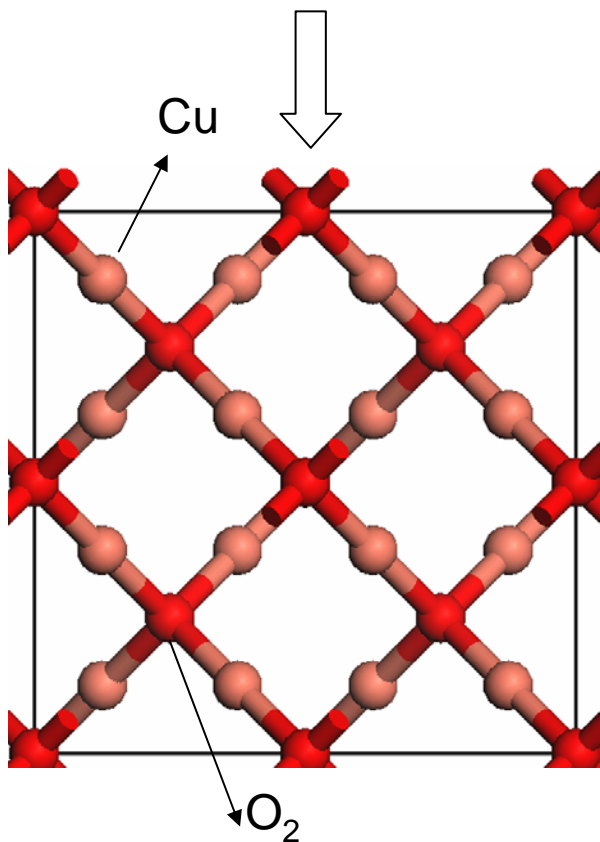


Band structure for  $\text{Cu}_2\text{O}$

# Why $\text{Cu}_2\text{O}$ has small band gap?

Atomic structure of stoichiometric  $\text{Cu}_2\text{O}$  with a  $(2 \times 2 \times 2)$  unit cell

Red = oxygen, pink = copper



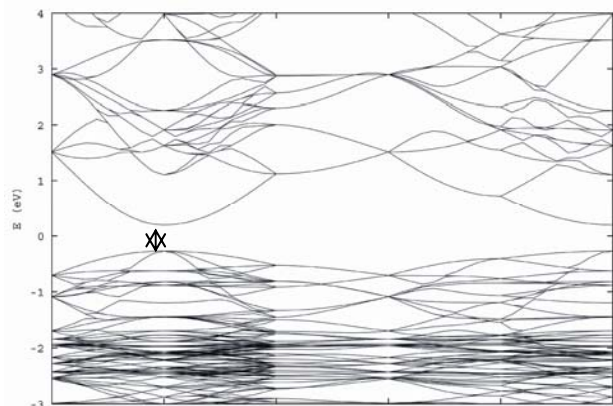
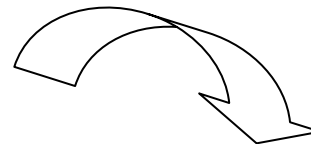
*Two interpenetrating Cu-O-Cu networks, but not bonded !  
(one light coloured and the other dark coloured)*

**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*

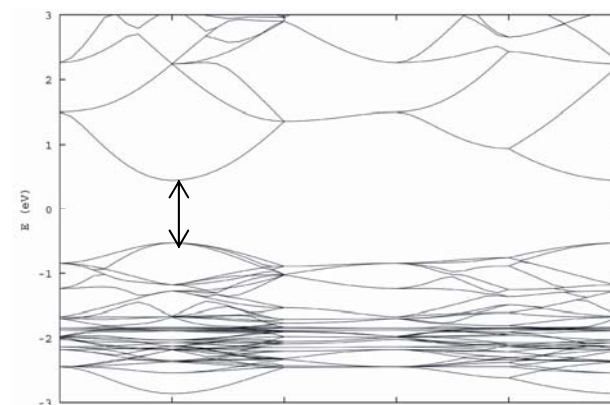
# Why $\text{Cu}_2\text{O}$ have small band gap?

- Remove 1  $\text{Cu}_2\text{O}$  network, but keep stoichiometry



Band structure for  $\text{Cu}_2\text{O}$

-Band gap increased to 1eV



Band structure for  $\text{Cu}_2\text{O}$  with one network removed.

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

*-Motivation for studying alloys of  $\text{Cu}_2\text{O}$ , e.g.  $\text{CuAlO}_2$ ,  $\text{SrCu}_2\text{O}_2$*

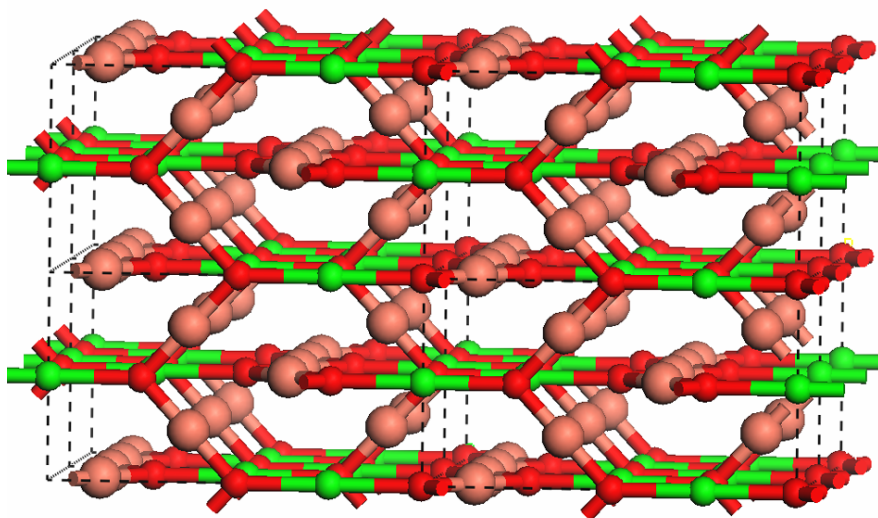
*M. Nolan et al, Chem Mat, 2008, 20, 5522; H. Kawazoe et al Nature 389, 939, 1997, A .Buljan, et al. Chem. Mater. 2001, 13, 338, X. Nie et al PRB, 65, 075111 ,2002)*



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

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

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



Pink: Copper

Red: Oxygen

Green: Alkaline Earth

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

$\text{MCu}_2\text{O}_2$ : Cu-Cu interactions are along 1-dimensional ribbons  $\rightarrow$  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 SrCu<sub>2</sub>O<sub>2</sub>?

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<sub>2</sub>O<sub>2</sub> series

-Structure

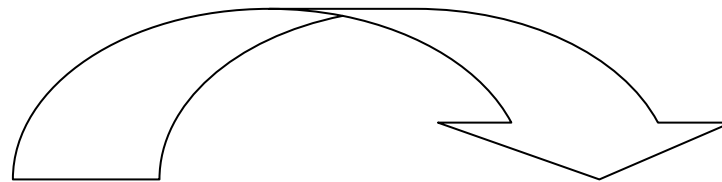
-Stability

-Band gap

-Effective hole masses

Computed lattice constants:

MCu <sub>2</sub> O <sub>2</sub>	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<sub>2</sub>O<sub>2</sub> 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*

# MCu<sub>2</sub>O<sub>2</sub> chemical stability

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

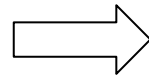
$$\Delta E = E(\text{MCu}_2\text{O}_2) - [E(\text{Cu}_2\text{O}) + E(\text{MO})]$$

-E(MCu<sub>2</sub>O<sub>2</sub>)-total energy of the bulk alloy,

-E(Cu<sub>2</sub>O) and E(MO) total energy of bulk Cu<sub>2</sub>O and the bulk alkaline earth oxide in the rock salt structure

## Computed $\Delta E$

MCu <sub>2</sub> O <sub>2</sub>	$\Delta E$ [eV]
Mg	+14 eV
Ca	+0.7 eV
Sr	-0.8 eV
Ba	-1.0 eV



- MgCu<sub>2</sub>O<sub>2</sub> and CaCu<sub>2</sub>O<sub>2</sub> are unstable
- SrCu<sub>2</sub>O<sub>2</sub> and BaCu<sub>2</sub>O<sub>2</sub> are stable.

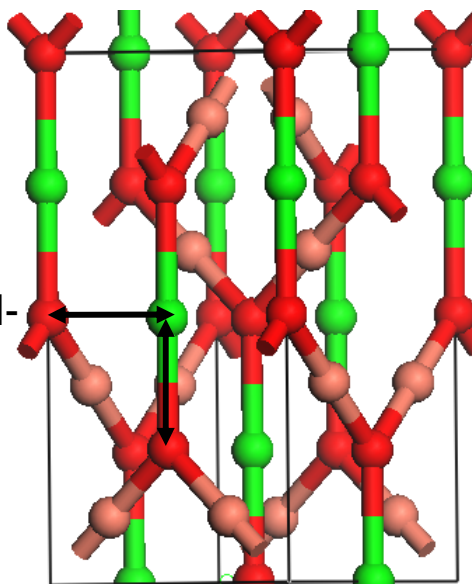
# MCu<sub>2</sub>O<sub>2</sub> chemical stability

R. Kucharski et al J.of Thermal Analysis and Calorimetry, 2000, 219/G. Moiseev et al. Thermochim. Acta, 1998, 318, 201/O. Vikhрева et al. Ceramics International, 1999, 25, 153 → have studied thermodynamic properties of MCu<sub>2</sub>O<sub>2</sub>

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<sub>2</sub>O and MO)

Origin?

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



Two sets of M-O distances

Pink: Copper  
Red: Oxygen  
Green: Alkaline Earth

Alloy	M <sup>2+</sup> -O in MCu <sub>2</sub> O <sub>2</sub> / Å	M <sup>2+</sup> -O in MO / Å
MgCu <sub>2</sub> O <sub>2</sub>	1.95, 2.57	2.10
CaCu <sub>2</sub> O <sub>2</sub>	2.27, 2.63	2.40
SrCu <sub>2</sub> O <sub>2</sub>	2.44, 2.72	2.58
BaCu <sub>2</sub> O <sub>2</sub>	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*

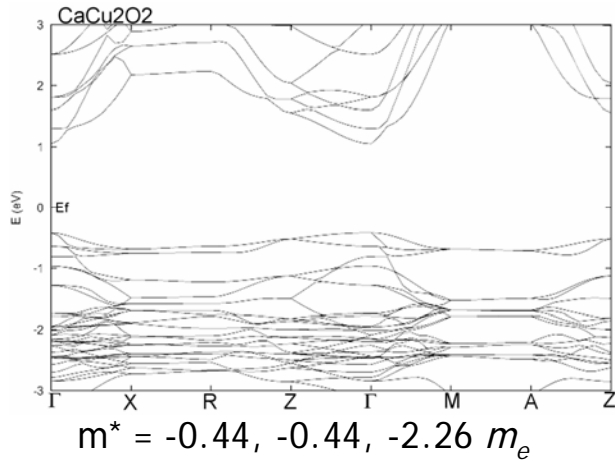
*Ba-O distances similar to Ba-O distances in BaO*

# MCu<sub>2</sub>O<sub>2</sub> Band Structure and Effective hole masses

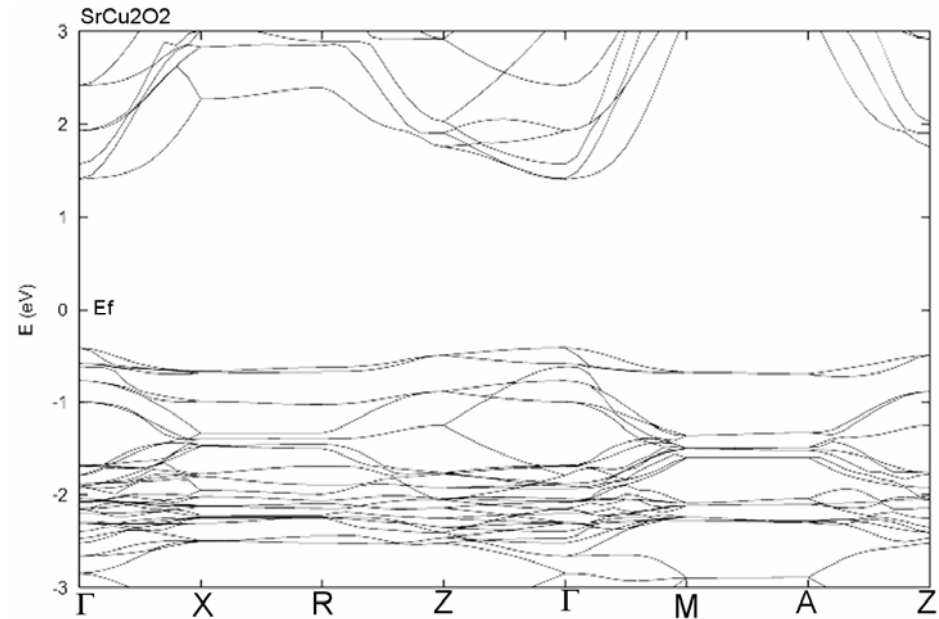
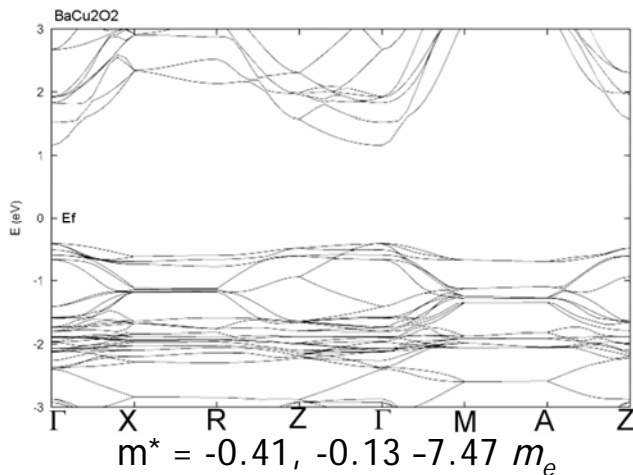
MgCu<sub>2</sub>O<sub>2</sub> (0.98 eV)

CaCu<sub>2</sub>O<sub>2</sub> (1.47 eV)

SrCu<sub>2</sub>O<sub>2</sub> (1.82 eV)



BaCu<sub>2</sub>O<sub>2</sub> (1.57 eV)



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

→  
Increasing band energy

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

# Origin of p-type conductivity?

In  $\text{Cu}_2\text{O}$ : 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

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

For  $\text{SrCu}_2\text{O}_2$ ?

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

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

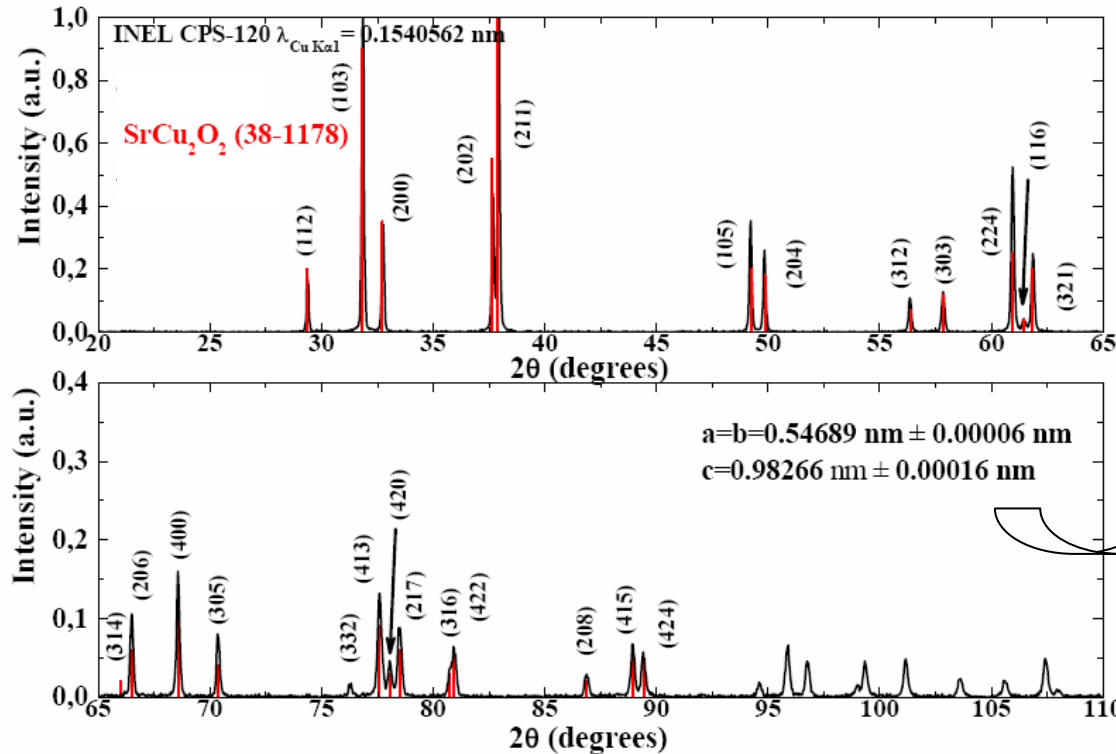
*This model appears to be general for copper oxides*

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

With Cu vacancy in  $\text{SrCu}_2\text{O}_2$ : Band gap ↗ 1.88 eV

$m^* = -6.66, -0.91, -1.48$

# Microstructural properties of bulk SrCu<sub>2</sub>O<sub>2</sub>



*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<sub>2</sub>O<sub>2</sub>. The ticks correspond to the theoretical peak positions and peak intensities of the crystalline phases from the JCPDS-ASTM databases listed on the upper figure*

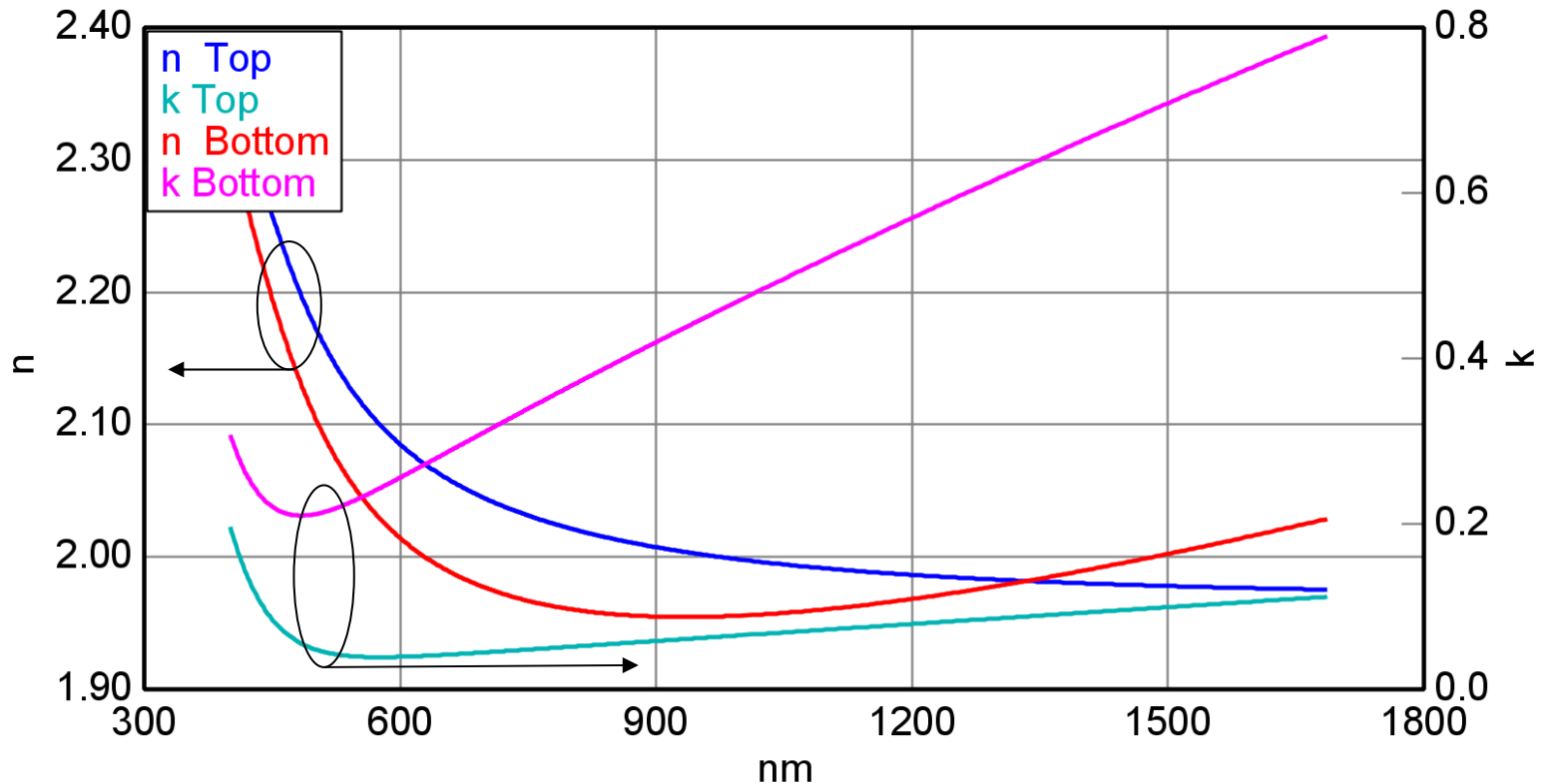
# Optical properties of SrCu<sub>2</sub>O<sub>2</sub>

- Scarce information available and no report on optical constants so far
- Optical band gap reports:
  - SrCu<sub>2</sub>O<sub>2</sub> and K doped SrCu<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> :  $E_g=3.00$  eV, PES and IPES spectroscopy\*\* (\*\*H.Ohta, J. Appl. Phys., 91, 5, 3074, 2002)
  - Bulk polycrystalline SrCu<sub>2</sub>O<sub>2</sub>:  $E_g= 3.35$  eV , spectroscopic ellipsometry (*This work*)



# SrCu<sub>2</sub>O<sub>2</sub> optical constants

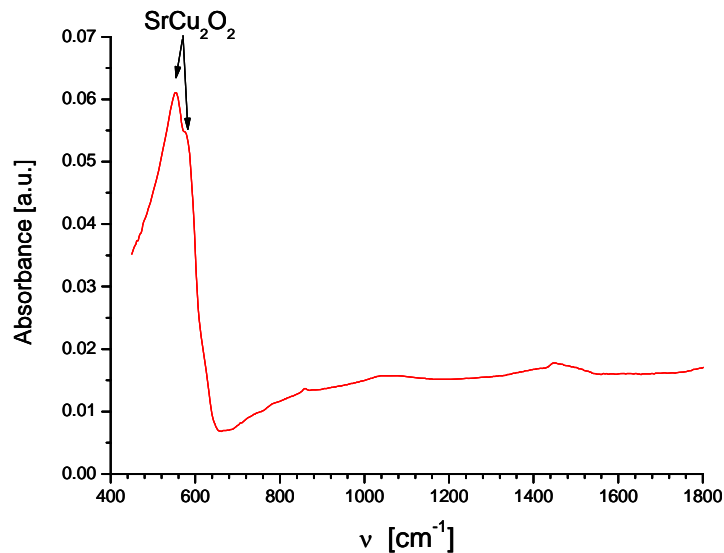
Optical constants SrCu<sub>2</sub>O<sub>2</sub>



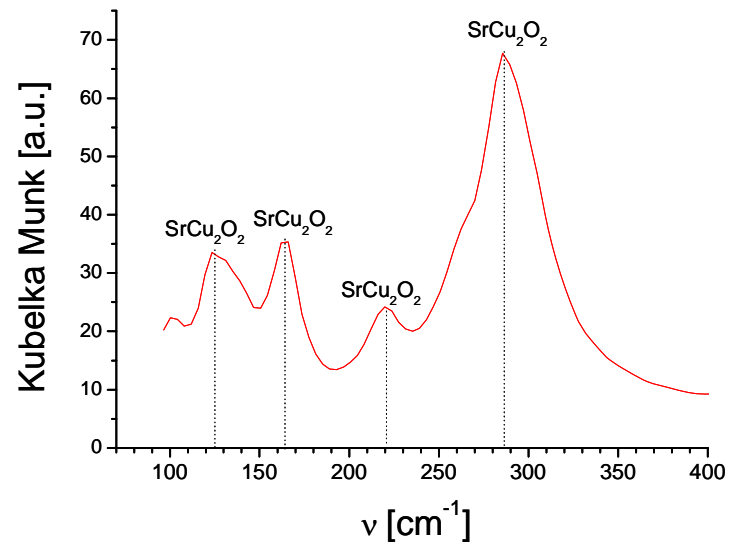
PLD deposition on Si substrates,  $T_{\text{dep}}=300^{\circ}\text{C}$ ,

# Tetragonal SrCu<sub>2</sub>O<sub>2</sub> Infrared active modes: bulk

Infrared active modes assigned for tetragonal SrCu<sub>2</sub>O<sub>2</sub>: 123, 166, 221, 289 and 579 cm<sup>-1</sup>



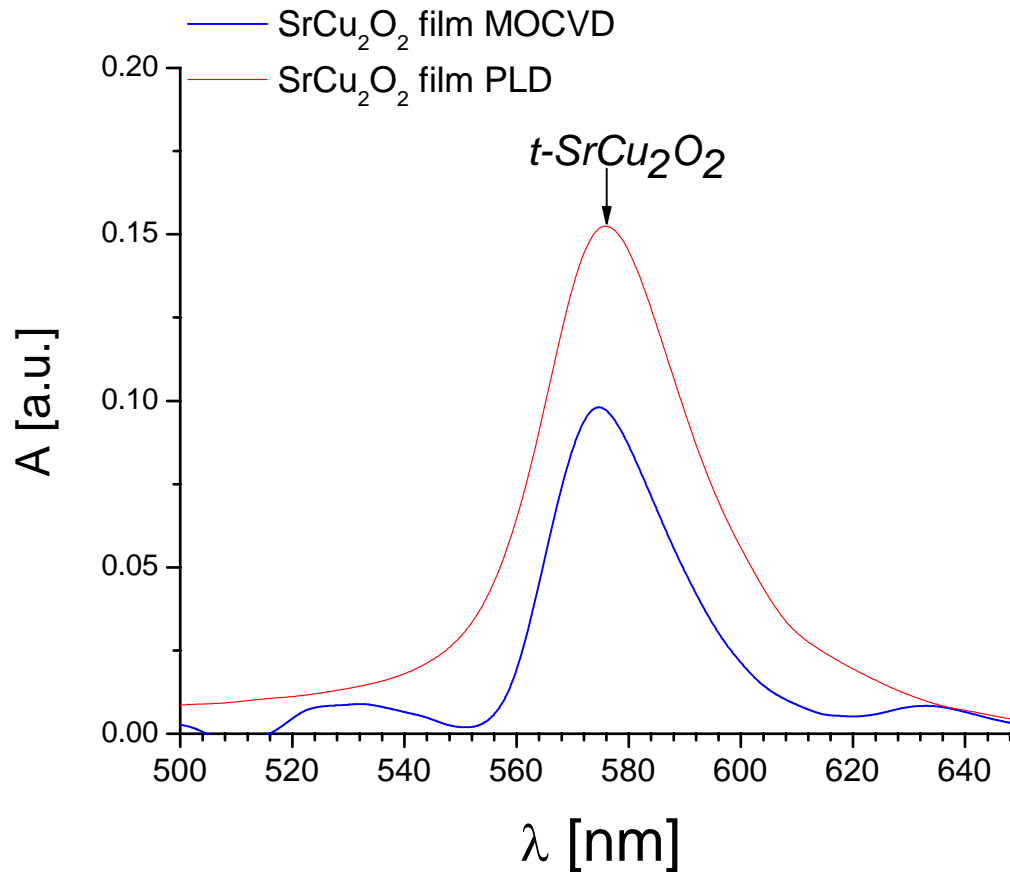
Mid-IR absorbance spectra of polycrystalline SrCu<sub>2</sub>O<sub>2</sub> powder measured by ATR technique. Spectral resolution 4 cm<sup>-1</sup>, 256 scans co-added. A



Far-IR DRIFT spectra of SrCu<sub>2</sub>O<sub>2</sub> powder (supplied by Umicore). Spectral resolution 8cm<sup>-1</sup>, 100 scans co-added.

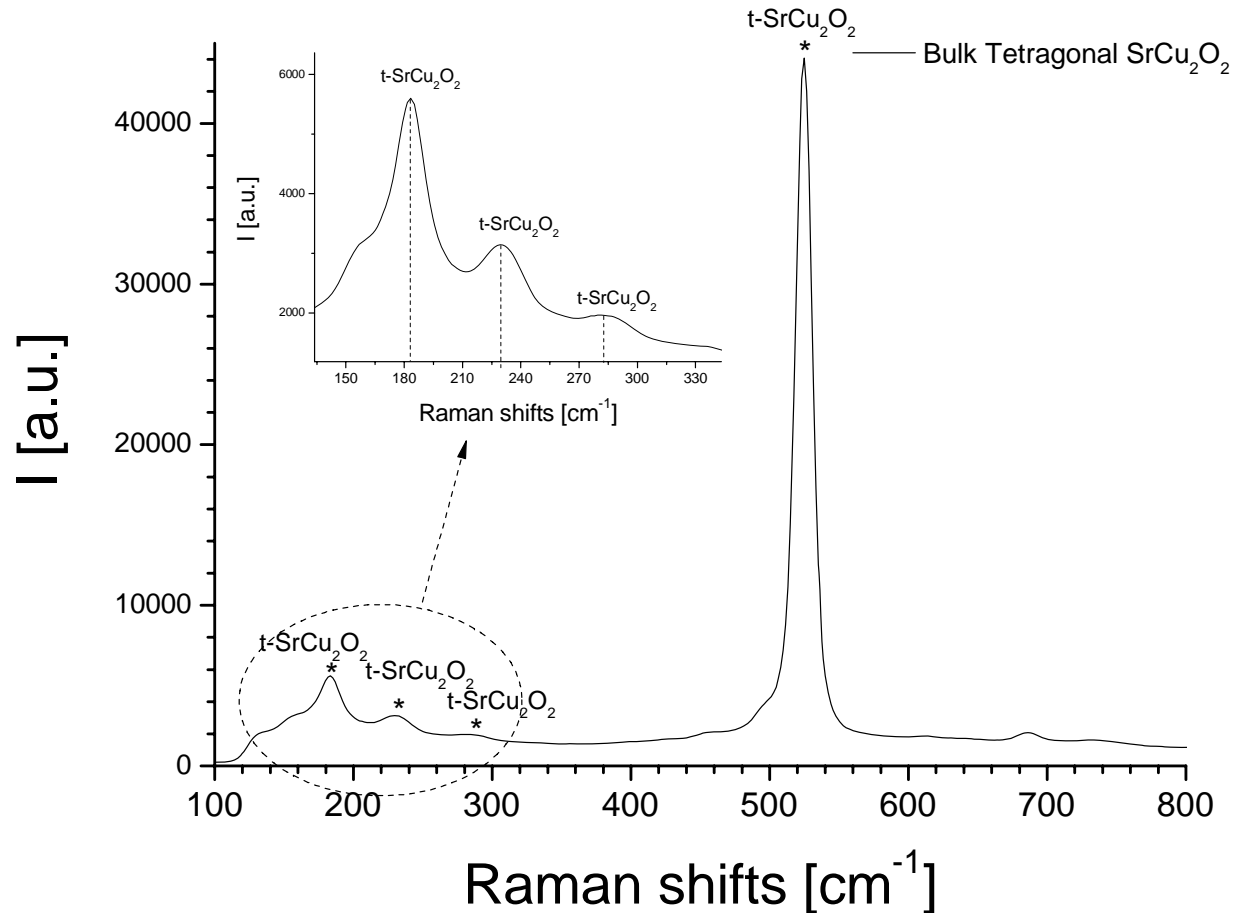
*Five infrared active modes assigned for tetragonal SrCu<sub>2</sub>O<sub>2</sub>*

# t-SrCu<sub>2</sub>O<sub>2</sub> thin films: Infrared fingerprints



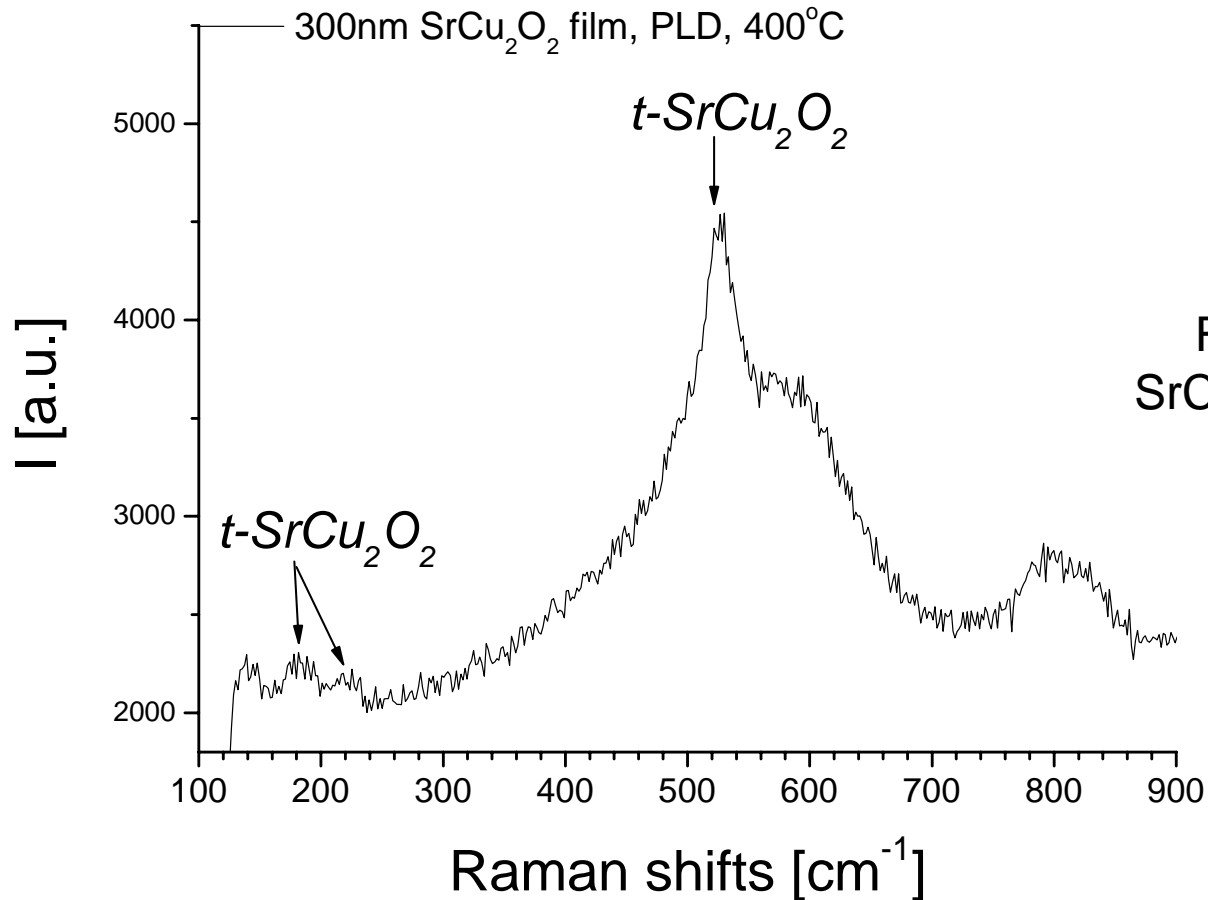
t-SrCu<sub>2</sub>O<sub>2</sub> fingerprint at 575cm<sup>-1</sup> (579cm<sup>-1</sup> in the bulk)

# Tetragonal $\text{SrCu}_2\text{O}_2$ Raman active modes: bulk



*Four Raman active modes assigned for  $t\text{-SrCu}_2\text{O}_2$ : 183, 231, 284, 530  $\text{cm}^{-1}$*

# t-SrCu<sub>2</sub>O<sub>2</sub> thin film: Raman characterisation

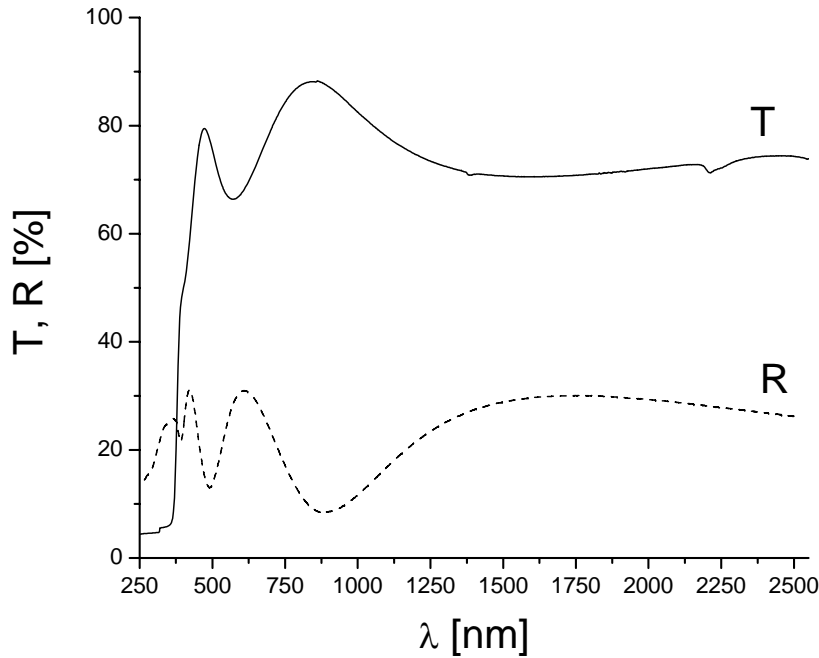


Raman highly sensitive to SrCu<sub>2</sub>O<sub>2</sub> films crystalline quality

SrCu<sub>2</sub>O<sub>2</sub> thin films, PLD, 400°C

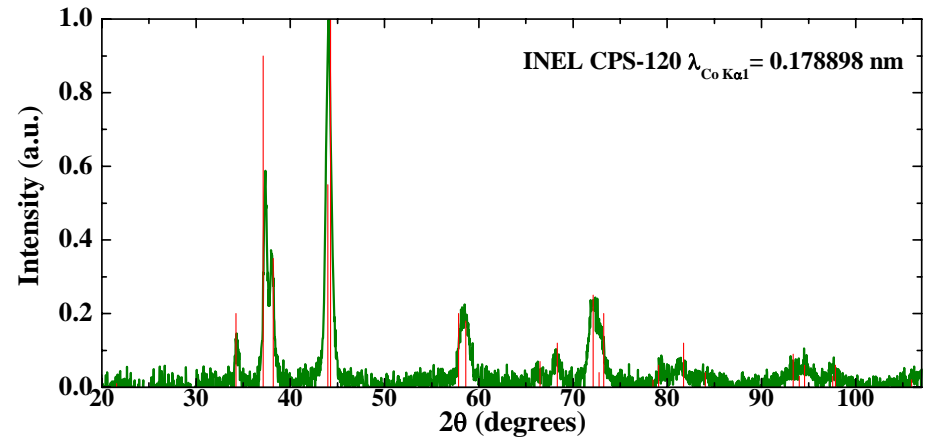
# Optical transparency of PLD SrCu<sub>2</sub>O<sub>2</sub> films

*High transparency in Vis-NIR spectral range*



Optical transmission and reflectance spectra of PLD SrCu<sub>2</sub>O<sub>2</sub> thin films (200 nm thick, T<sub>dep</sub>=300°C)

Low surface roughness: 3nm



XRD patterns for the PLD SrCu<sub>2</sub>O<sub>2</sub> thin films (200nm thick) . The red lines show the position and the intensities for SrCu<sub>2</sub>O<sub>2</sub> (JCPDS-ICDD: 38-1178)

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<sub>2</sub>O<sub>2</sub>
- Raman highly to disorder into SrCu<sub>2</sub>O<sub>2</sub> films crystallinity (*better than XRD*)
- First determination on optical constants
- Understanding the mechanism enhancing Cu vacancies generation will enable improvement in SCO electrical properties

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- Odette Chaix, Jean-Luc Deschanvres<sup>5</sup>

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<sup>3</sup>GEMaC, CNRS-Université de Versailles-Saint-Quentin, France;

<sup>4</sup>Umicore Group Research & Development, Belgium

<sup>5</sup>IESL FORTH, Crete, Greece;

<sup>6</sup>LMGP, CNRS-INP Grenoble, France