Mapping of novel binary copper oxides with density functional theory modelling

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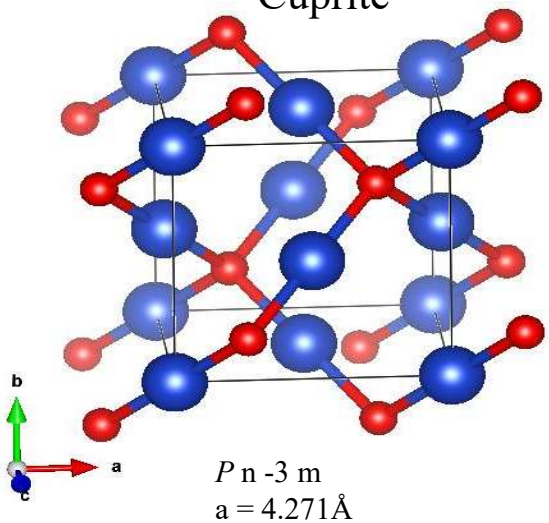
Introduction

- Binary copper oxides [Cu-O] have remarkable electronic and optical properties.
- Cu-O find numerous applications in photovoltaics and all-oxide electronics due to their abundance, low cost and non-toxic nature that makes Cu-O highly attractive for further exploration.
- ***Our Goal -*** To predict new stable binary Cu-O phases using density functional theory (DFT) and Evolutionary Algorithm (EA) methods.

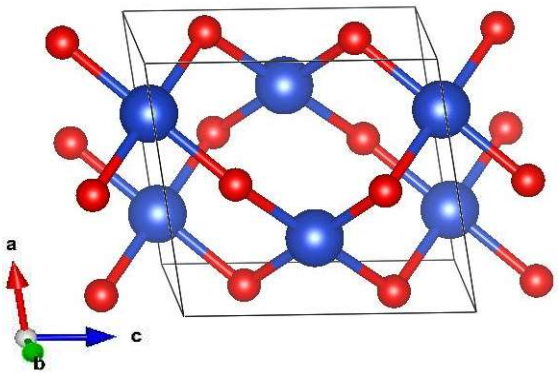
Known binary Cu-O

$Cu^{I}_{2}O$[1]
Cuprite



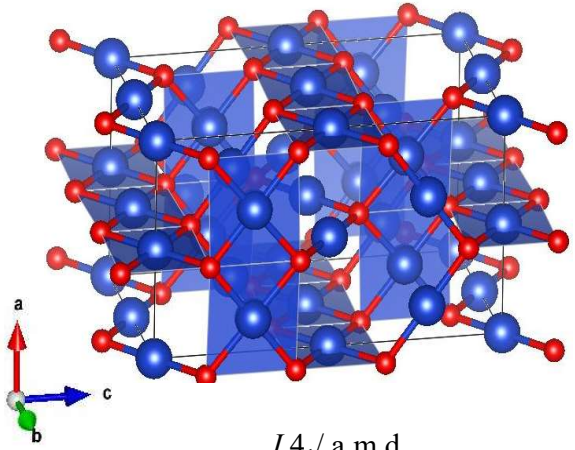
P n -3 m
a = 4.271Å

$Cu^{II}O$[2]
Tenorite



*C*2/c
a = 4.691Å, b = 3.417Å,
c = 5.13Å, β = 99°

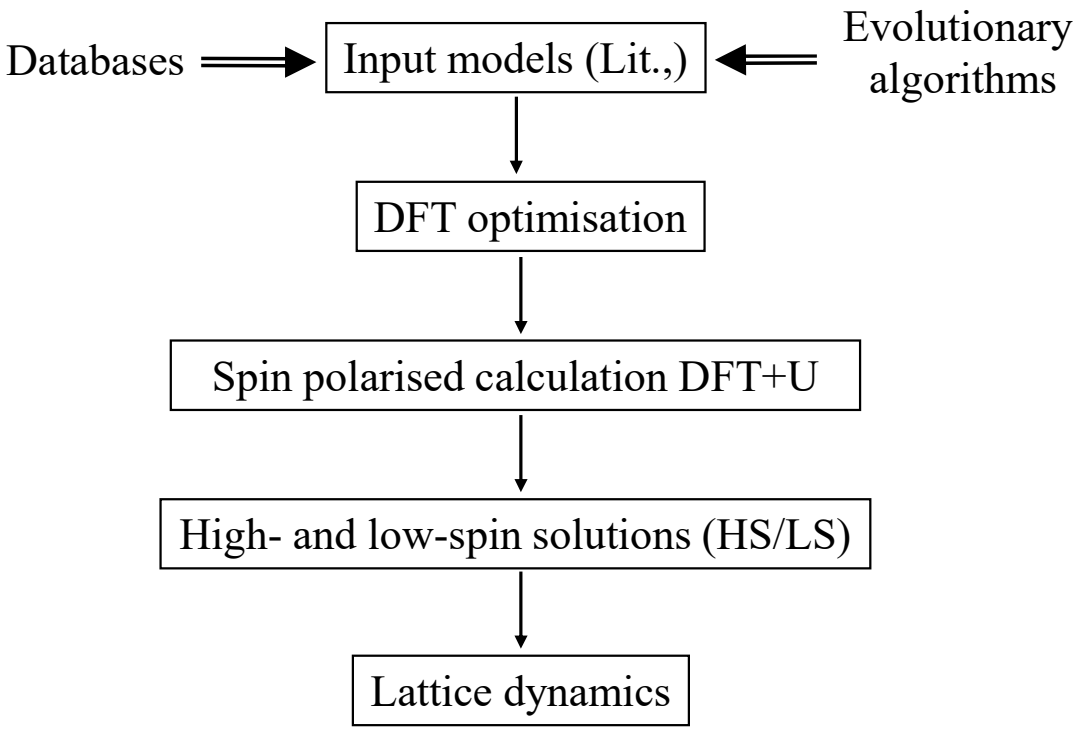
$Cu^{I}_{2}Cu^{II}_{2}O_{3}$[3]
Paramelaconite



I 4_1/ a m d
a = b = 5.818Å,
c = 9.894Å

[1] Benxian L et.al, J. Solid State Chem., 184, 2097 (2011)
[2] Chaudhary N et.al, Solid State Commun., 247, 36 (2016)
[3] Morgan P E D et.al, J. Solid State Chem., 121, 33 (1996)

Computational procedure

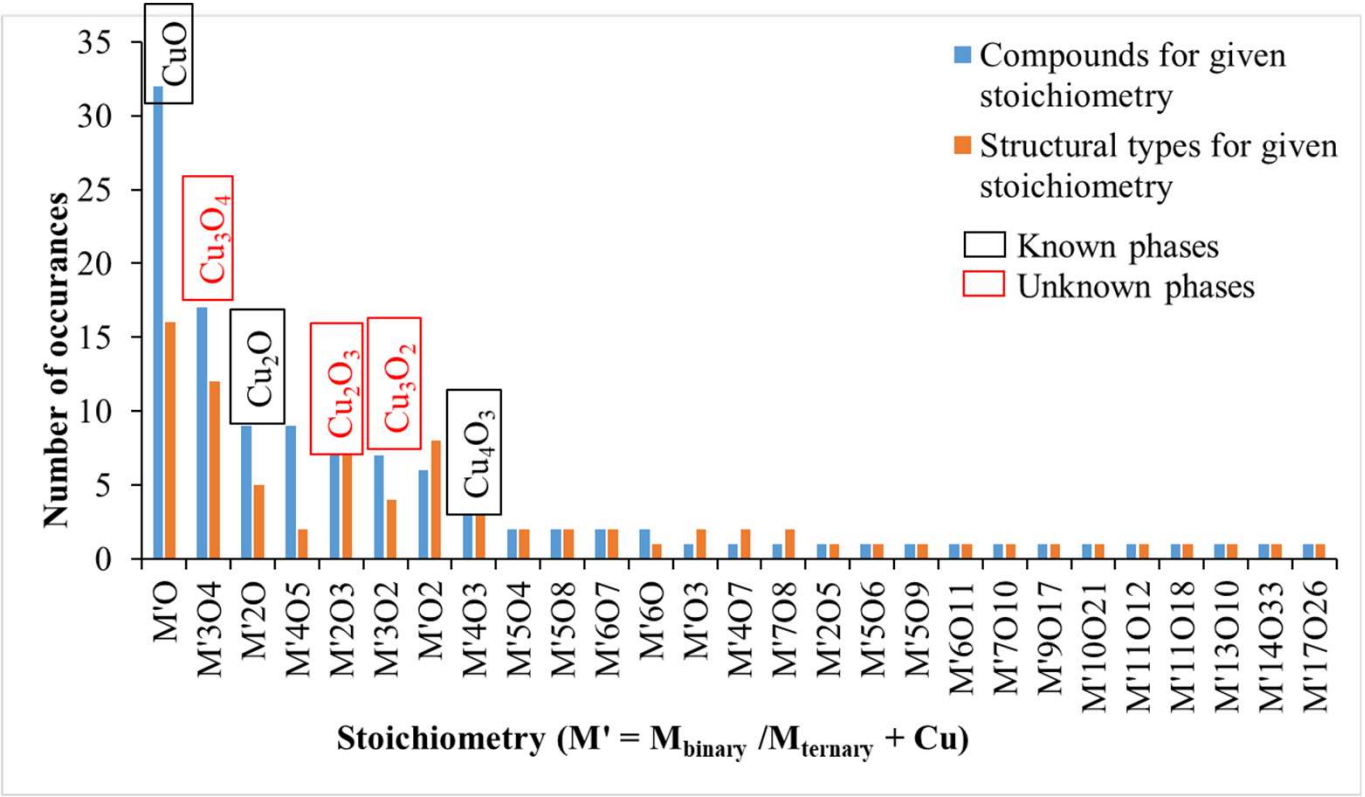


Calculation details

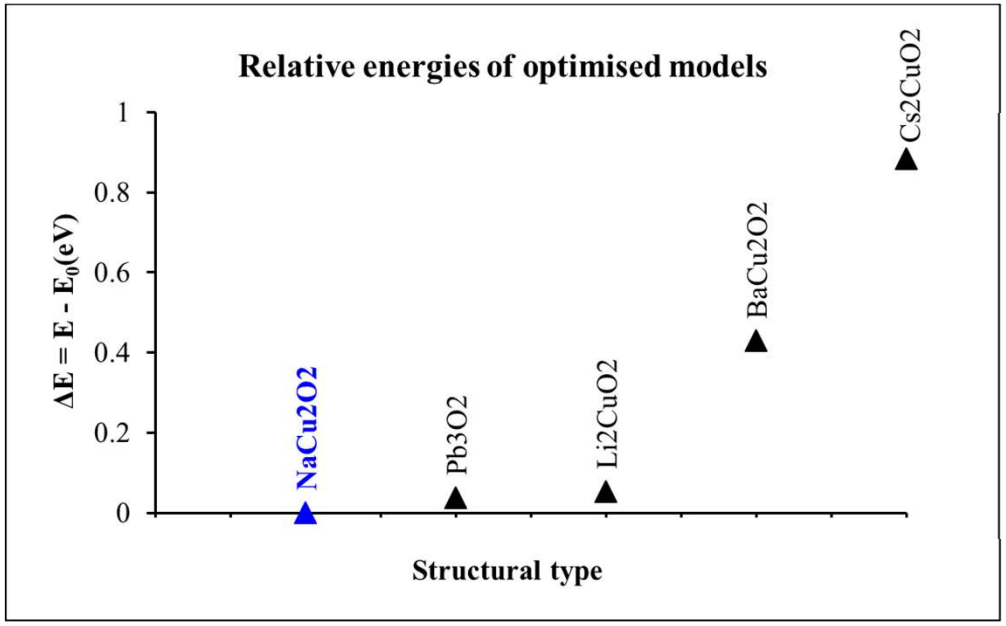
- DFT method for structure optimization (VASP program).
- Details of the DFT calculations: PBEsol functional, planewave cut-off 520eV.
- Electron correlations handled with Liechtenstein approach: U_{Cu}=9eV, J_{Cu}=1eV.
- EA for the search of crystal structures (XtalOpt program[4]).
- Lattice dynamics calculations using program PHONOPY[5].

[4] Patrick A et.al, Comput. Phys. Commun., 222, 418 (2018)
[5] Togo A et.al, Scr. Mater., 108, 1 (2015)

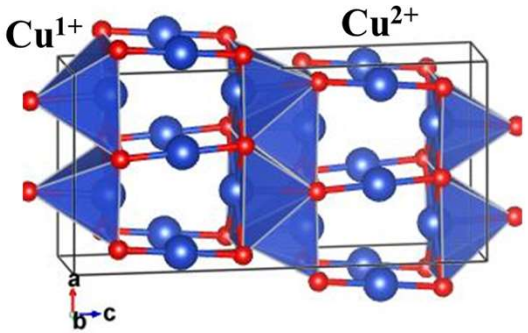
Strategy for the selection of input models

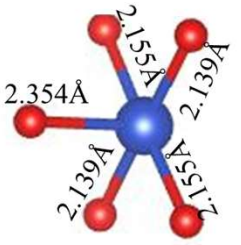


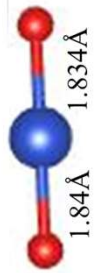
Cu_3O_2 Stoichiometry



$NaCu_2O_2$ Structural type





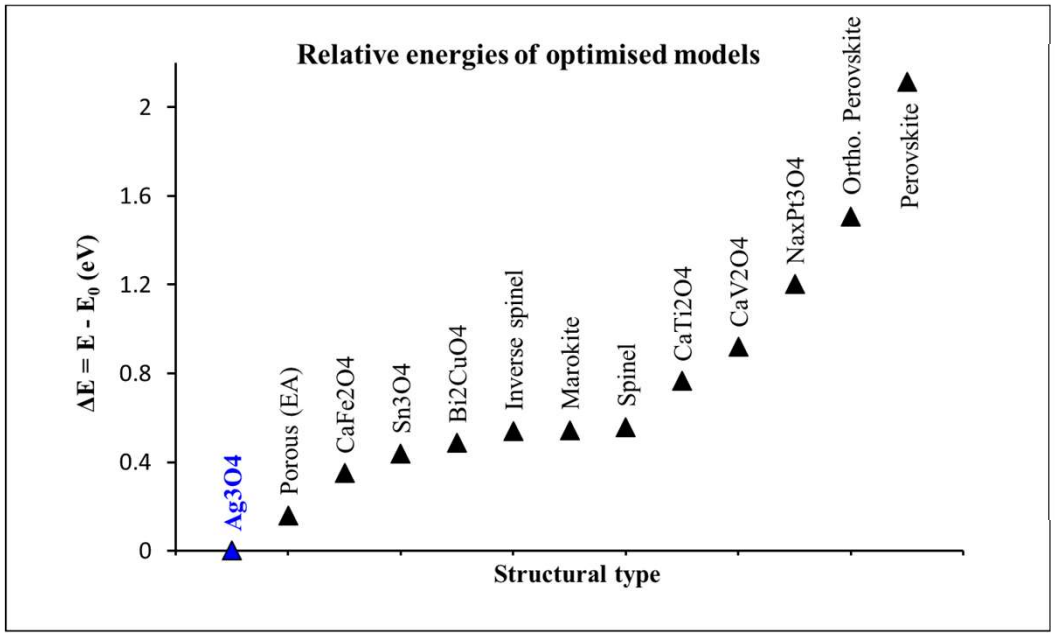


Cu^{1+} (0.030 mB)

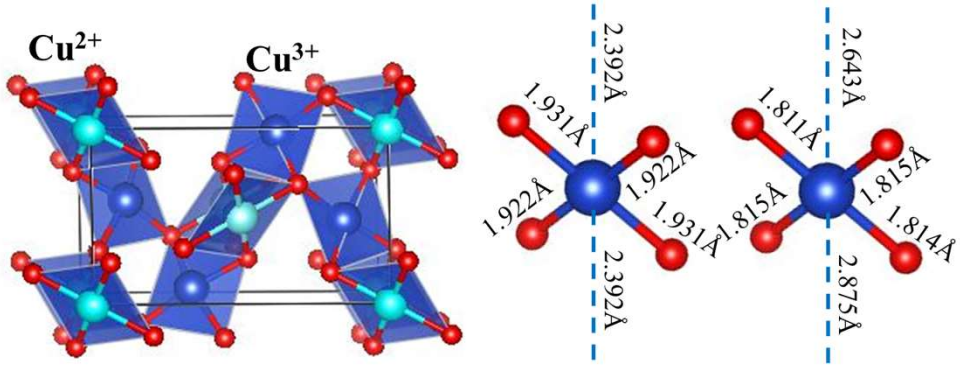
Cu^{2+} (0.633 mB)

P n m a
a = 5.896Å, *b* = 2.827Å, *c* = 2.139Å

Cu_3O_4 Stoichiometry



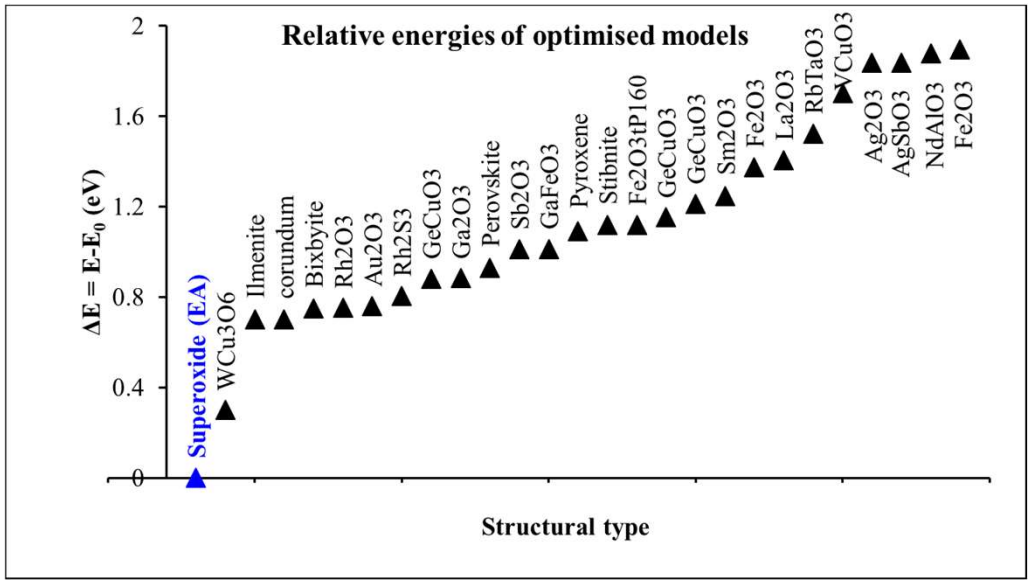
Ag_3O_4 Structural type



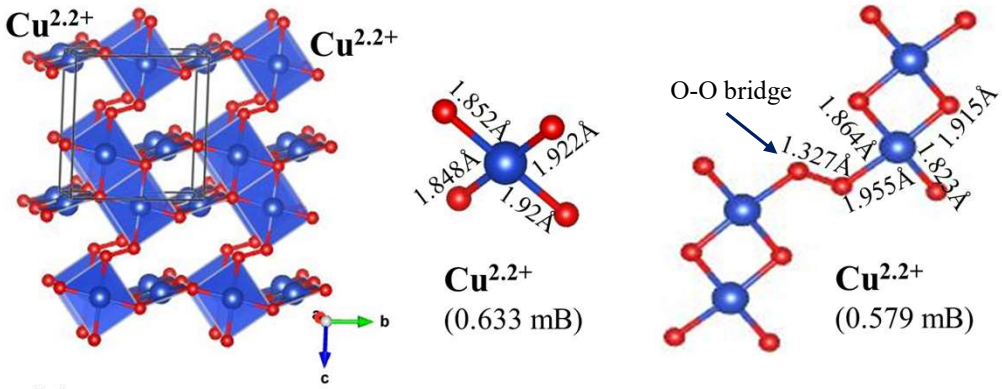
P 1 2_1 / c 1
a = 3.298Å, b = 8.454Å,
c = 5.005Å, β = 102.9°

Calculated both HS and LS solutions. Only LS solution is stable.

Cu_2O_3 Stoichiometry



Superoxide(EA) Structural type



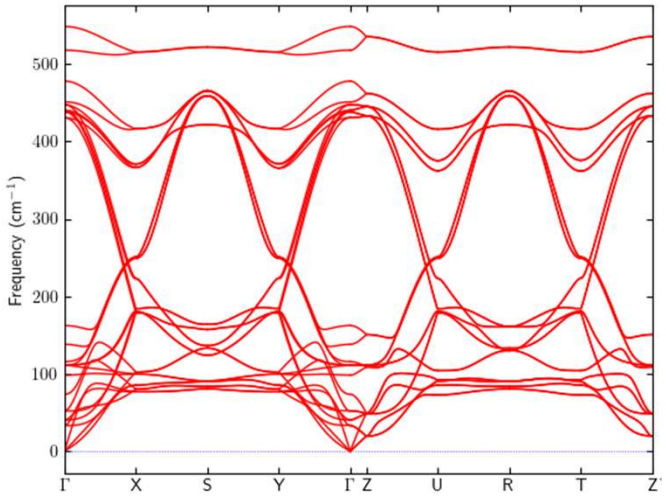
P 1
a = 2.789Å, b = 5.957Å,
c = 6.578Å, α = 93°; β = 102.9°; γ = 94°

Compound (spin)	a (Å)	b (Å)	c (Å)	V/Z $(Å)^3$	ΔE/Z (eV)	Mag. (m_B)
Superoxide(EA) (FM)	2.794	5.927	6.582	50.661	0.006	0.626
Superoxide(EA) (AFM)	2.789	5.957	6.578	50.886	0.000	+0.627 -0.581

Impact of lattice dynamics on the stability of the models

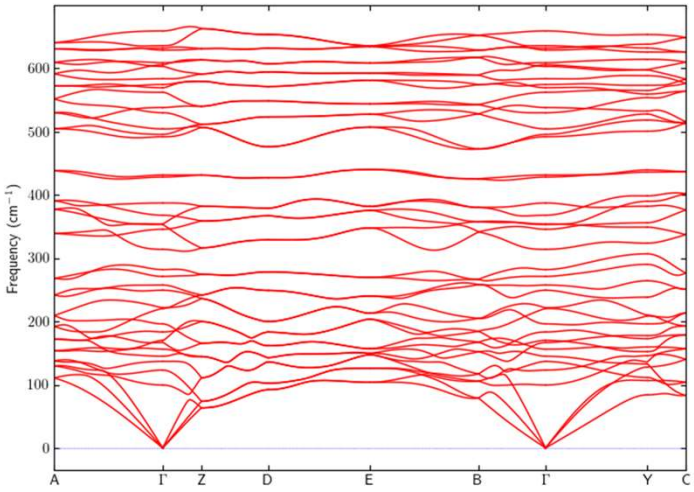
Phonon dispersion curves

Cu_3O_2



Na_2CuO_2 structure type

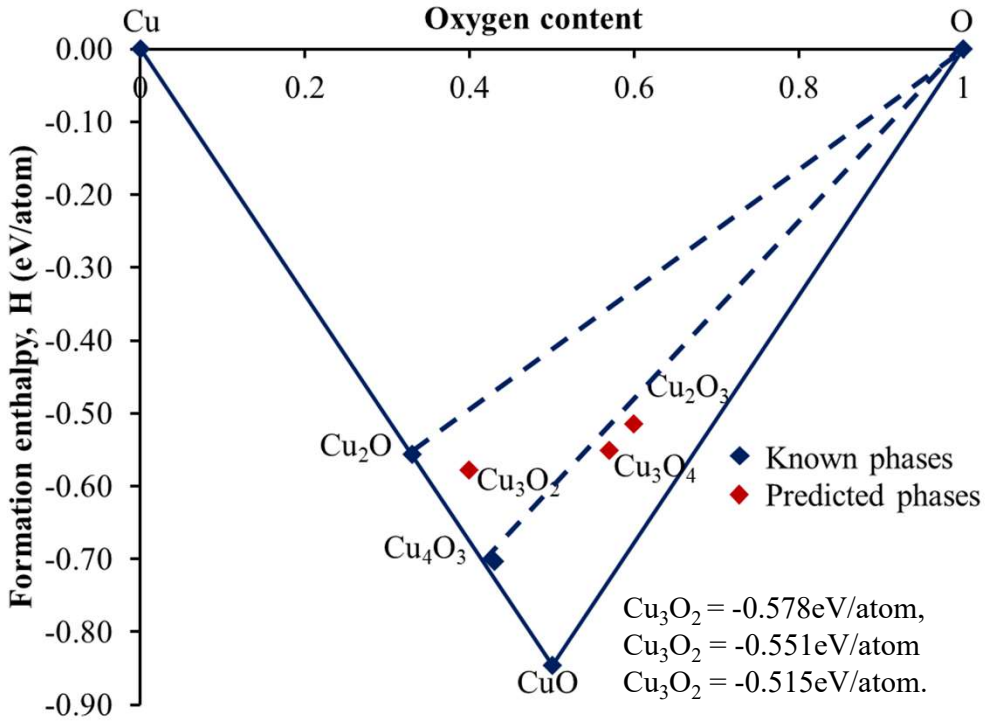
Cu_3O_4



Ag_3O_4 structure type

Convex Hull

- Thermodynamically, Convex Hull represents the enthalpy.
- Correctly predicted the stability of existing phases.
- 3 new Cu-O phases are stable with respect to elements Cu, O and Cu_2O phase.
- Cu_3O_4 and Cu_2O_3 are stable with respect to Cu_4O_3.
- 3 new phases are metastable in respect to CuO phase.



Conclusions

- Crystal structures of 3 new Cu-O compounds are predicted – Cu_3O_2, Cu_3O_4 and Cu_2O_3.
- Cu_3O_2 was predicted for Na_2CuO_2 type structure.
- Cu_3O_4 was predicted as a low spin Ag_3O_4 structural type.
- Cu_2O_3 was predicted as a AFM superoxide (EA) type.
- The new structure types found to be dynamically stable.
- Correctly predicted the stability of existing binary Cu-O phases.
- The newly predicted Cu-O phases are stable with respect to elements Cu, O and Cu_2O phase.
- Cu_3O_4 and Cu_2O_3 are stable with respect to Cu_4O_3.

Acknowledgements

The European Regional Development Fund, Research and Innovation Operational Programme, for project No. ITMS2014+: 313011W085.

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Thank you for your attention!