# First-principles exploration of thermodynamically stable Cs–O compounds

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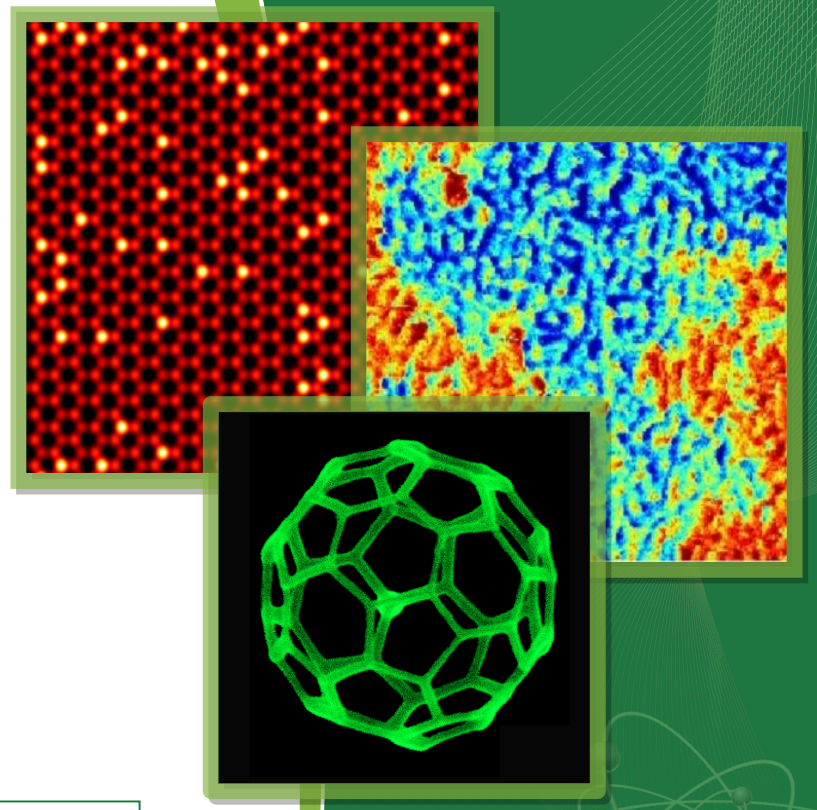
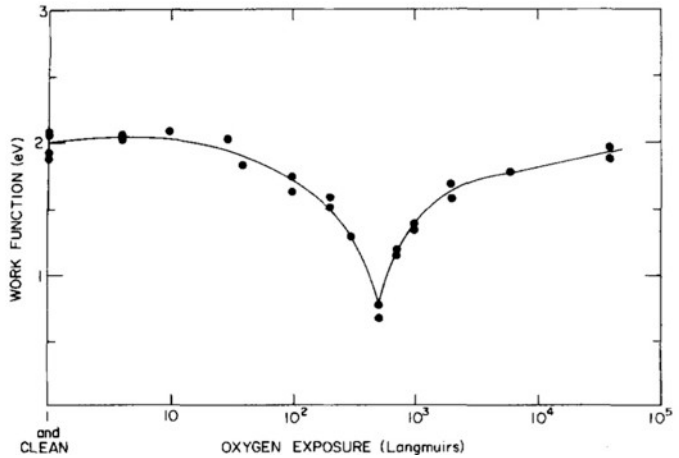


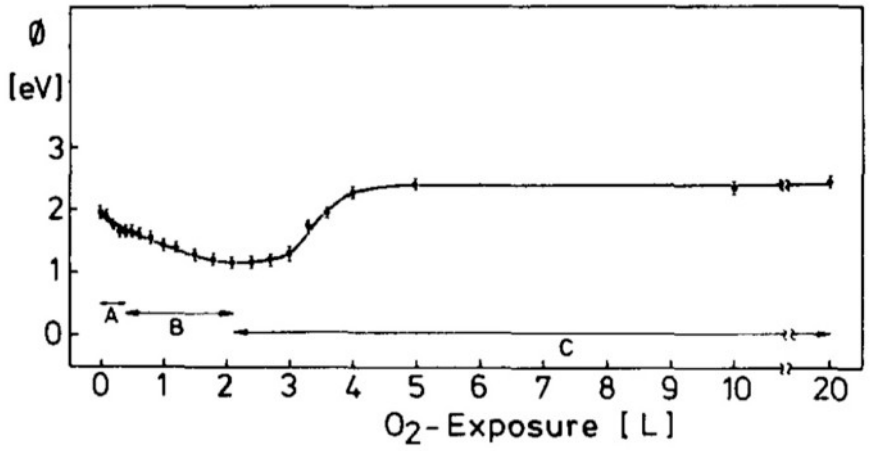
***Part of this work was performed at CNMS, a DOE Office of Science User Facility that provides free access if the intent is to publish. (cnms.ornl.gov)***

# Motivation: cesium oxides as a low work function material

- **Oxidation can significantly lower their work functions**




P. E. Gregory, et al. Appl. Phys. 46, 3525 (1975)




B. Woratschek, et al. J. Chem. Phys. 86, 2411 (1987)

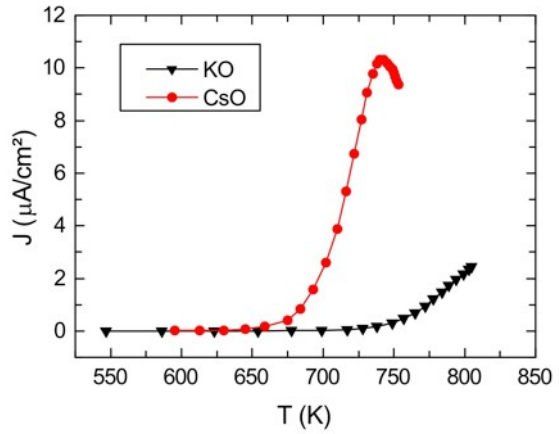
Different oxides are introduced.
Exact composition was not provided.

A: Cs → $Cs_{11}O_3$
B: $Cs_{11}O_3$ → $Cs_2O_2$
C: $Cs_2O_2$ → $CsO_2$

# Application

- **Recent applications as a low work function coating**

  - Improvement in thermionic emission in thermionic energy convertor




| | $\phi_{PE}$ (eV) | $\phi_{TE}$ (eV) |
|---|---|---|
| K/O:Si | $1.73 \pm 0.16$ | $1.75 \pm 0.28$ |
| Cs/O:Si | $1.66 \pm 0.27$ | $1.72 \pm 0.20$ |

* work function of Silicon : 4.85 eV

V. Giorgis, et al., J. Appl. Phys. 120, 205108 (2016)

  - Improvement in electron injection in solar cells

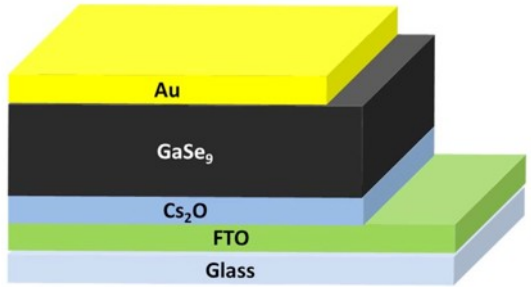
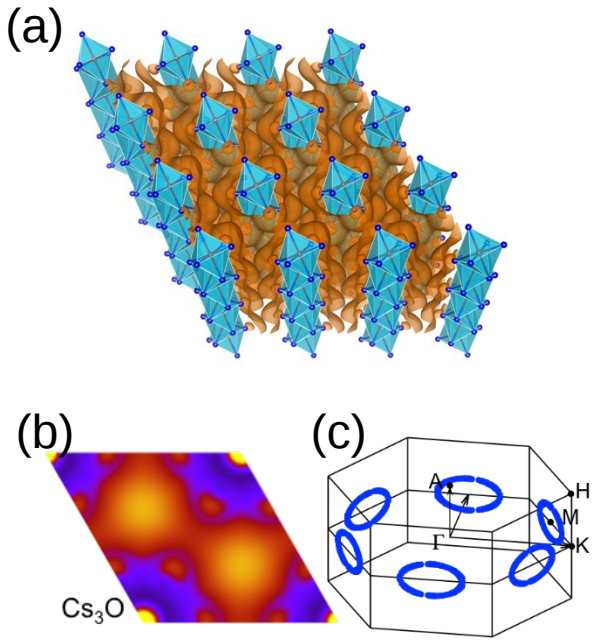



Fig. 1. Device structure of FTO/$Cs_2O$/$GaSe_9$/Au solar cells.

A. Hoff, et al., Solar Energy Materials and Solar Cells 171, 1 (2017)

# Discovery of a new class of 1D electrides with nontrivial band topology: $Cs_3O$




(a-b) Charge density distribution of newly identified electrides, $Cs_3O$ based on 1D nanorods, where anionic electrons near the Fermi level are highly concentrated in the inter-rod cavity space, and the electronic band structure (c) shows topologically protected Dirac node line loops.

- **Electrides are ionic compounds where the anions are electrons**, making them promising for chemical synthesis and electronics.
- First-principles density functional theory calculations are coupled to a materials database search to analyze key materials' properties and to investigate their detailed band structures.
- **The new class of 1D electrides** ($Cs_3O$ and $Ba_3N$) is the first electrides with **nontrivial band topology** presenting band inversion and topologically protected quantum states.
- Experimental synthesis is a challenge.

C. Park, S.W. Kim, M. Yoon, Phys. Rev. Lett. 120, 26401 (2018)

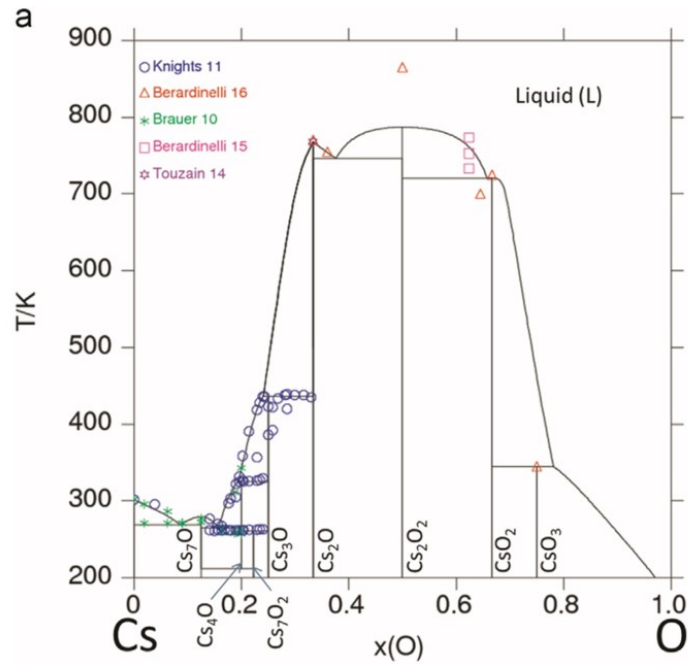
Talk presented by M. Yoon (K12.00010)

# Computational exploration of Cs-O: First-principles approach

- **Difficulties in experimental characterization of cesium oxides**
  - High air sensitivity (Low chemical stability)
  - Unusual large number of oxides
  - Poor crystallinity

- **Theoretical characterization**
  - First-principles density functional theory calculation (DFT) + global structure prediction with particle swarm optimization: (VASP + CALYPSO)
  - Exploring metastable crystal structures: $Cs_3O$, $Cs_2O$, CsO
  - Electronic structure analysis
  - Work function calculations

G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996)
Y. Wang, J. Lv, L. Zhu, and Y. Ma, Phys. Rev. B 82, 094116 (2010)

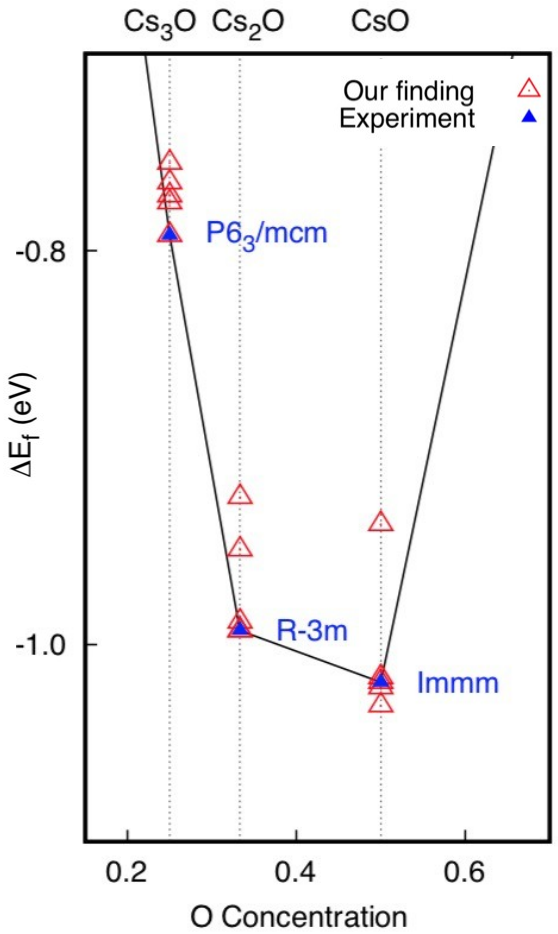



C. Guéneau and J. L. Flèche, Calphad 49, 67 (2015)

# Computationally identified metastable configurations

| Composition | Formation energy (eV) | Space group |
|---|---|---|
| $Cs_3O$ | -0.755 | $P2_1/m$ |
| | -0.765 | $Pmc2_1$ |
| | -0.772 | R-3 |
| | -0.775 | $Cmc2_1$ |
| | -0.792 | $P6_3/mcm$ |
| $Cs_2O$ | -0.925 | Pnnm |
| | -0.951 | Pmmn |
| | -0.988 | Fd-3m |
| | -0.992 | C2/m |
| | -0.992 | R-3m |
| CsO | -0.939 | Amm2 |
| | -0.970 | $P2_1/c$ |
| | -1.019 | Immm |
| | -1.021 | C2/m |
| | -1.031 | $P2_1/c$ |

Convex hull phase diagram

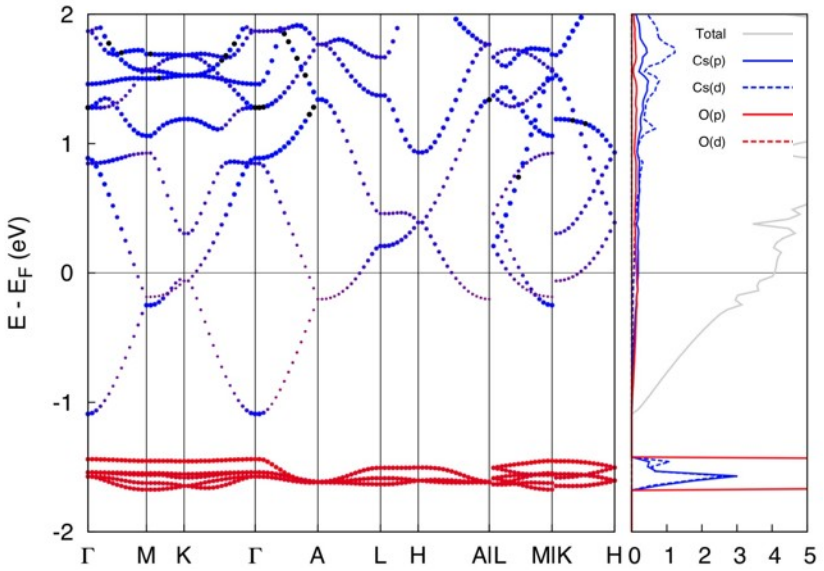


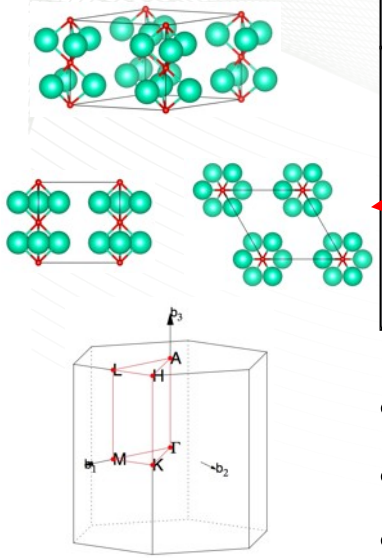

Formation Energy: $\Delta E_f = \dfrac{\left[E(Cs_xO_y) - \left\{x \times \dfrac{E(Cs)_{bcc}}{2} + y \times \dfrac{E(O_2)}{2}\right\}\right]}{(x+y)}$

- Our results agree well with the experimental data.
- Our computational approach identifies new crystal structure that is energetically more stable than the experimentally synthesized one.

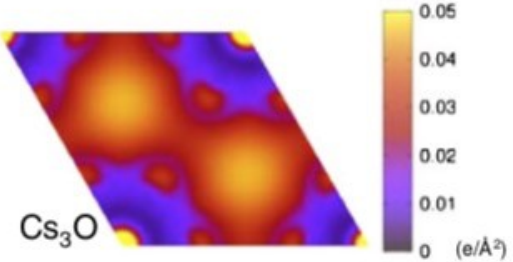
# Crystal structures and electronic properties : $Cs_3O$

$P6_3/mcm$ (193)



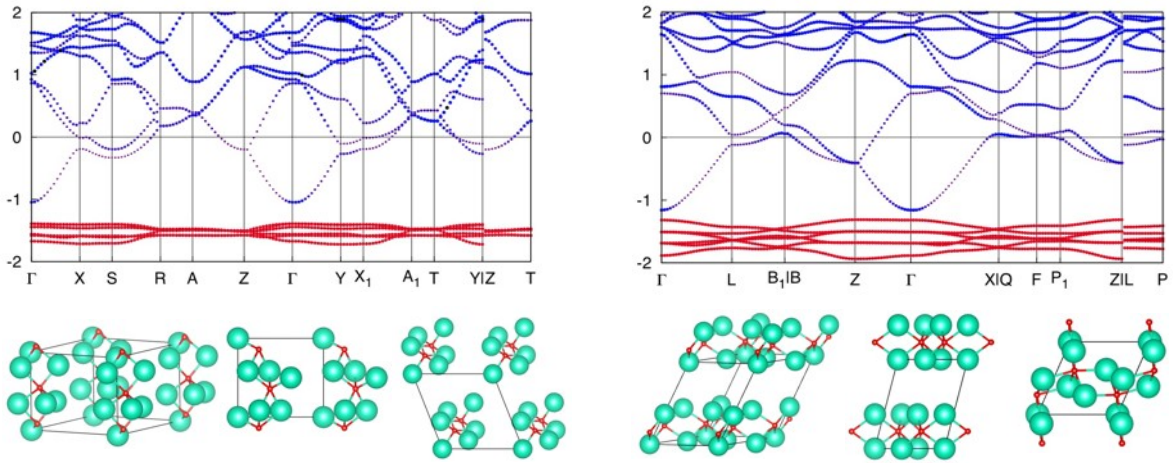
| Composition | Formation energy (eV) | Space group |
|---|---|---|
| $Cs_3O$ | -0.755 | $P2_1/m$ (11) |
| | -0.765 | $Pmc2_1$ (26) |
| | -0.772 | R-3 (148) |
| | -0.775 | $Cmc2_1$ (36) |
| | -0.792 | $P6_3/mcm$ (193) |




C. Park, et al., Phys. Rev. Lett.
120, 026401 (2018)

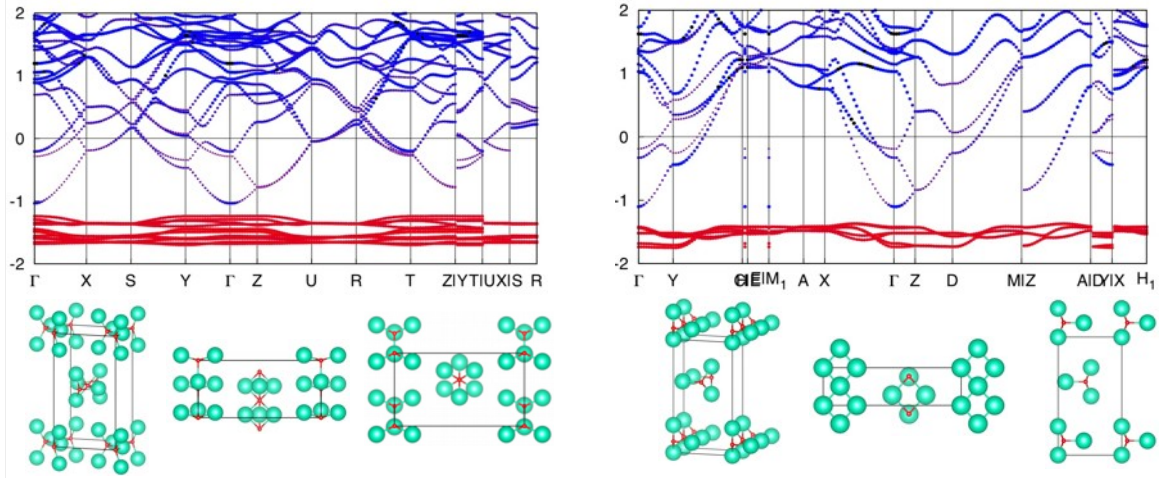
- New 1D based electride ($P6_3/mcm$)
- metals
- New 1D / 2D structures were identified.

$Cmc2_1$ (36)




R-3 (148)

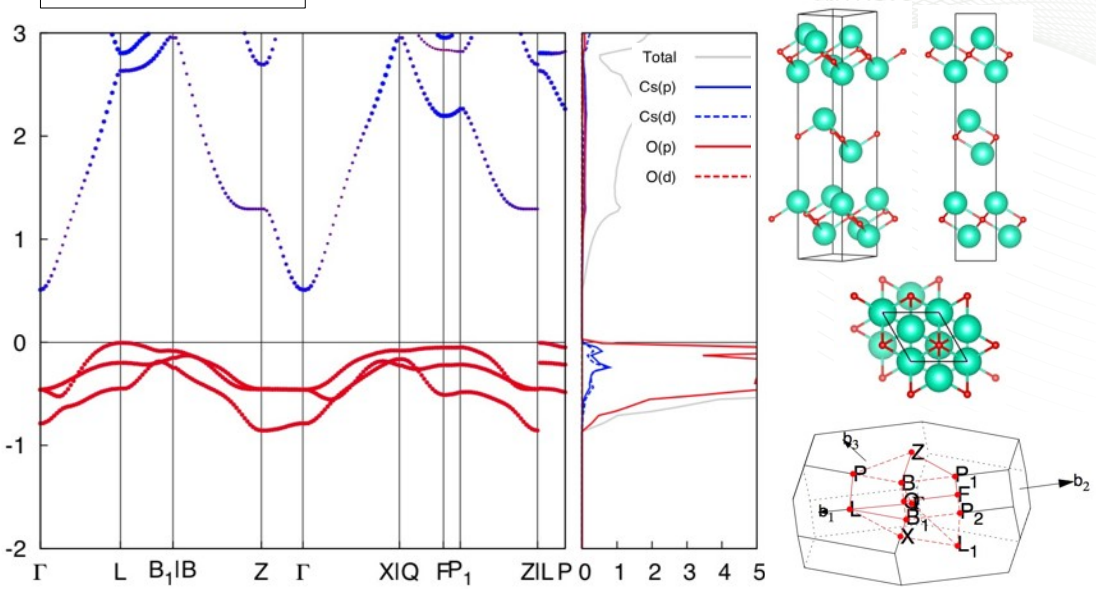
$Pmc2_1$ (26)




$P2_1/m$ (11)

# Crystal structures and electronic properties : $Cs_2O$

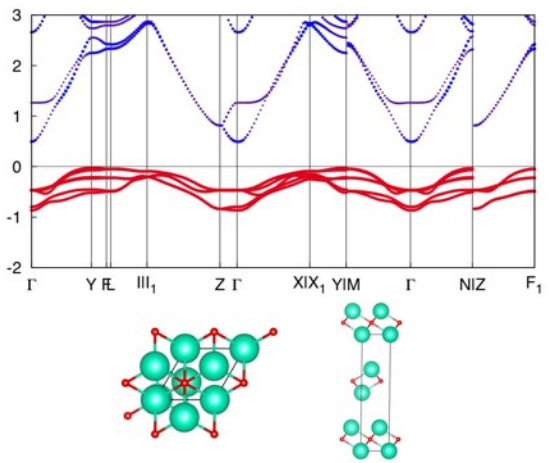
R-3m (166)



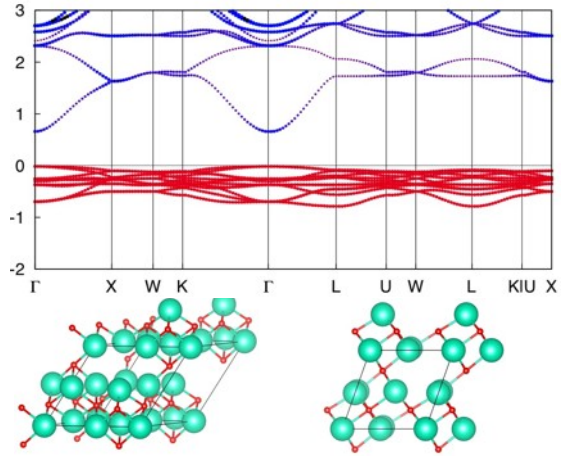

| Composition | Formation energy (eV) | Space group | Direct gap (eV) | Global gap (eV) |
|---|---|---|---|---|
| $Cs_2O$ | -0.925 | Pnnm (58) | 0.85 | - |
| | -0.951 | Pmmn (59) | 0.33 | - |
| | -0.988 | Fd-3m (227) | 0.67 | - |
| | -0.992 | Cm (8) | 0.96 | 0.52 |
| | -0.992 | R-3m (166) | 0.97 | 0.52 |

- $Cs_3O$ → $Cs_2O$: opening of band gaps (<1eV, PBE)
- High band dispersion of conduction bands governed by metallic Cs states
- 2D layered structures were identified.

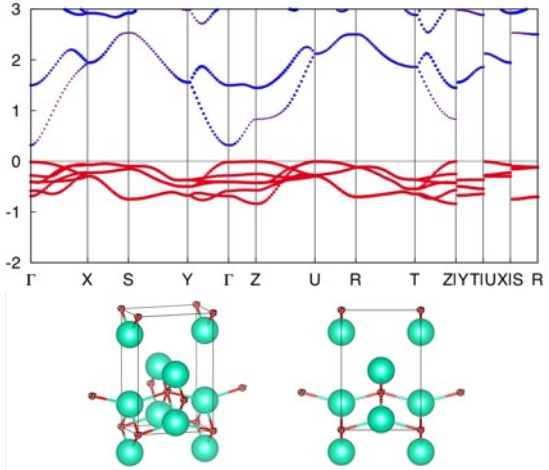
Cm (8)



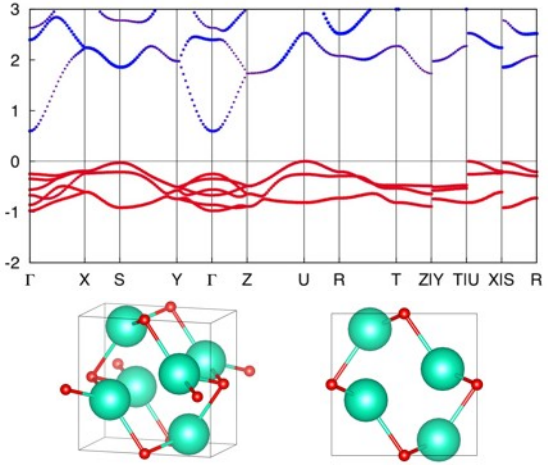

Fd-3m(227)




Pmmn

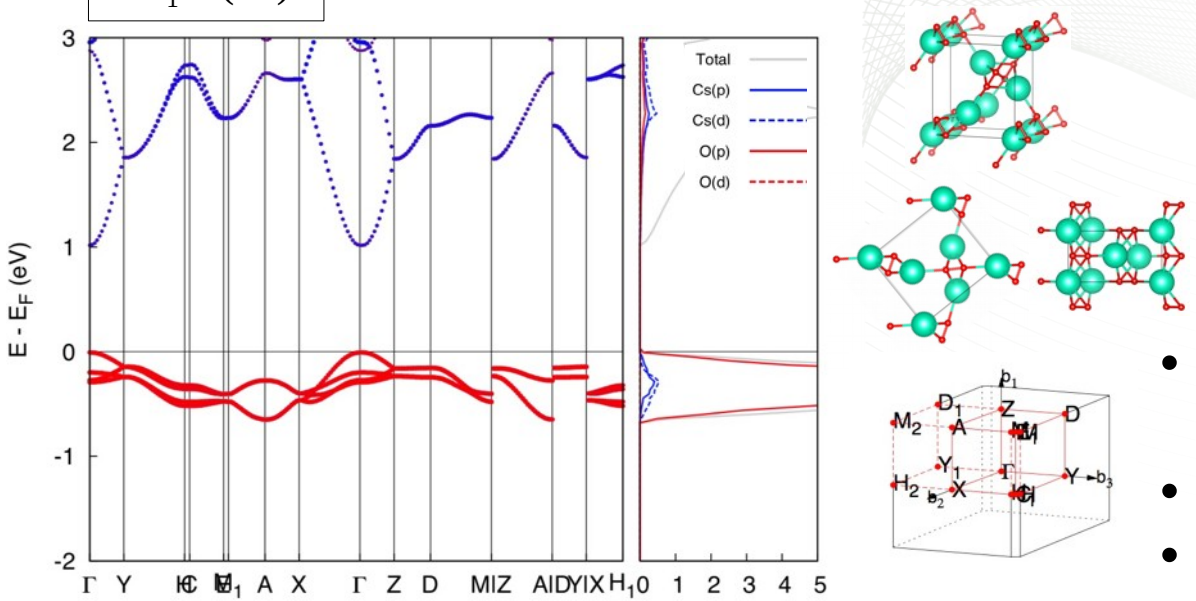



Pnnm



# Crystal structures and electronic properties : CsO

P2$_1$/c (14)

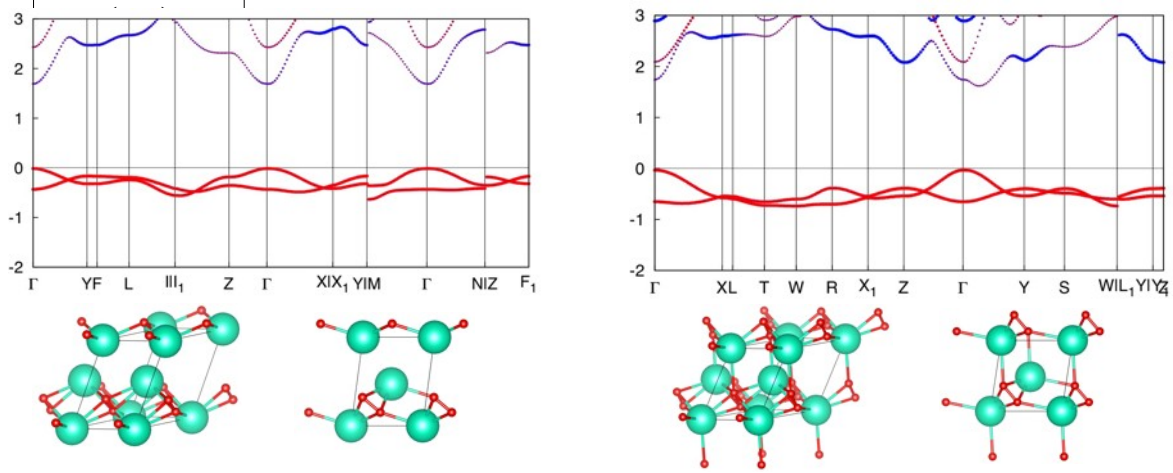





| Composition | Formation energy (eV) | Space group | Direct gap (eV) | Global gap (eV) |
|---|---|---|---|---|
| CsO | -0.939 | Amm2 (38) | 1.21 | 0.83 |
| | -1.017 | P2$_1$/c (14) | 1.92 | - |
| | -1.019 | Immm (71) | 1.71 | 1.65 |
| | -1.021 | C2/m (12) | 1.71 | - |
| | -1.031 | P2$_1$/c (14) | 1.02 | - |

- A noticeable hybridization between O and Cs states.
  : reduced band dispersion
- Band gaps further increase with O concentration: 1~2eV
- 2D layered structures were identified.

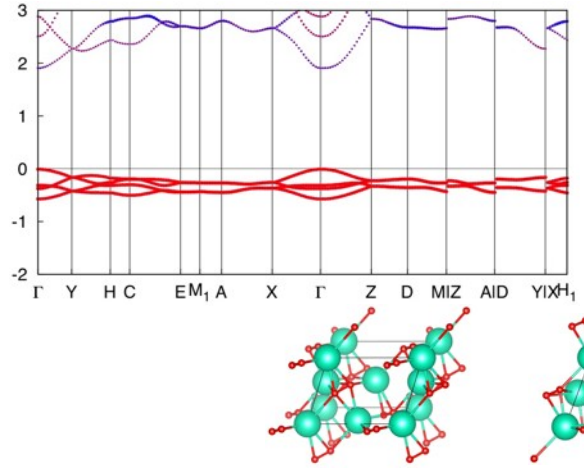
C2/m



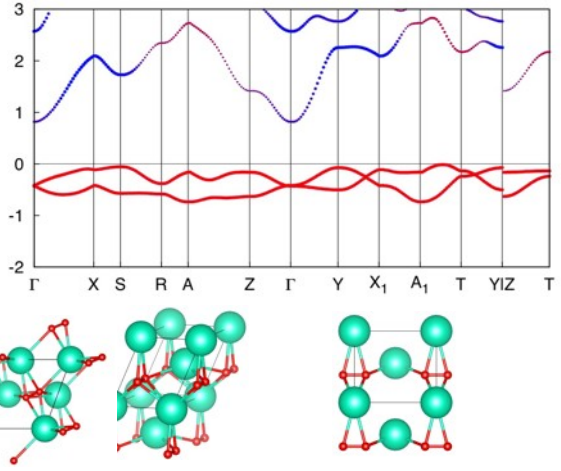
Immm (71)



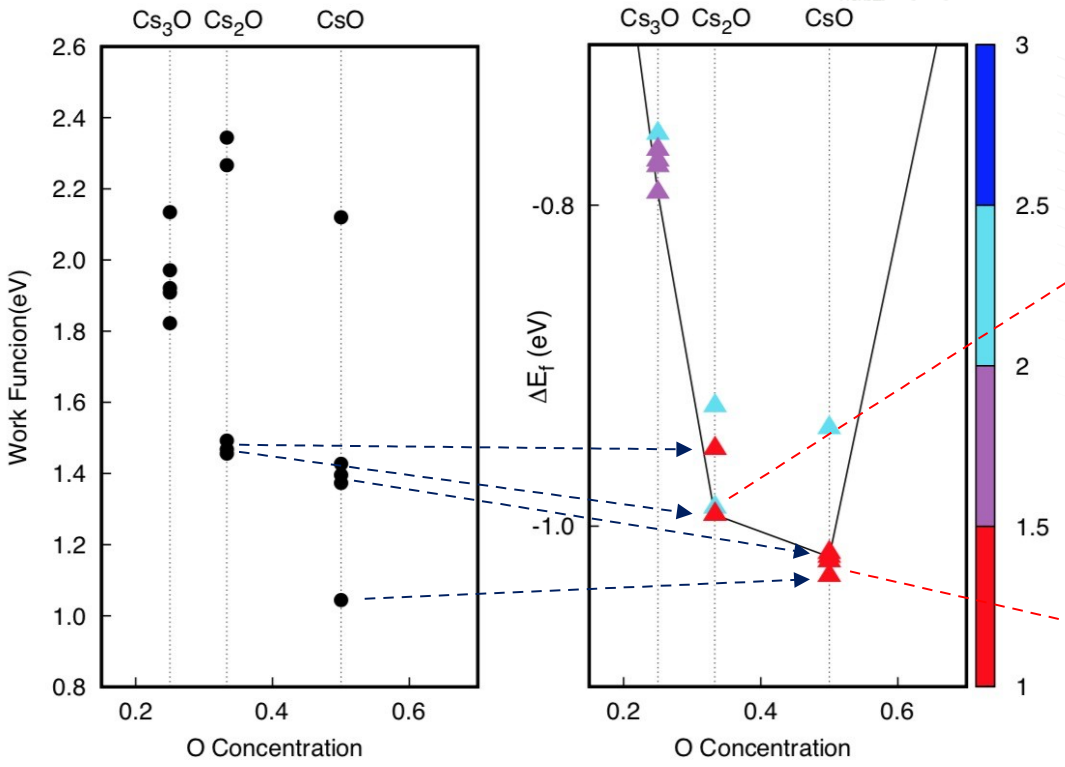
P2$_1$/c (14)

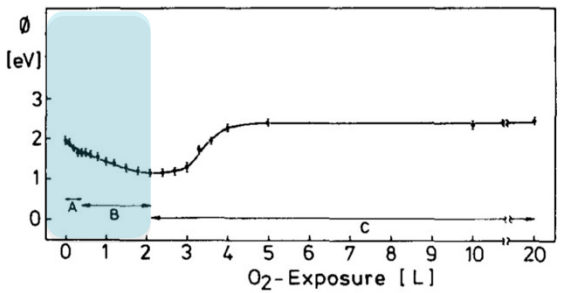


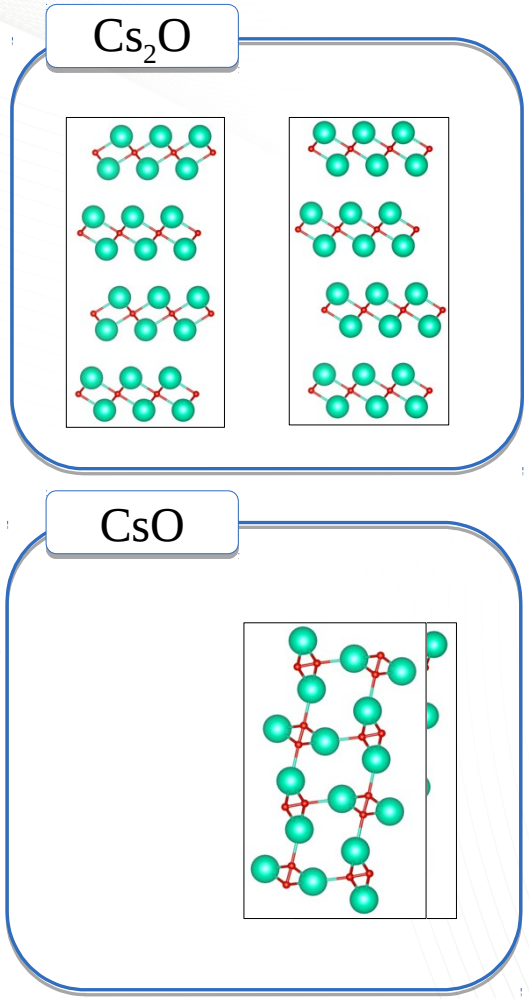
Amm2 (38)



# Work functions




- $Cs_2O$ and CsO compositions show low work function below 1.5 eV
- The change in the work function is in good agreement with experimental results.
- Newly found most stable structure of CsO turned out to have the lowest work function
- Configurations with low work function show 2D layered structure.

B. Woratschek, et al. J. Chem. Phys. 86, 2411 (1987)

# Summary

- Metastable structures of cesium oxides compounds($Cs_3O$, $Cs_2O$, CsO) were predicted and characterized by using PSO and DFT.

- $Cs_3O$ metastable structures show crystal and electronic structures that could be seen as electrides.

- Newly found most stable structure of CsO shows the lowest work function.

- Calculated work functions are in good agreement with the experimental results and structural condition that allows low work function is suggested.

# Center for Nanophase Materials Sciences

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### Proposals:

- Simple, two-page narrative
- Two general calls per year
- Short-term projects accepted continuously
- Joint proposals with neutron sources (SNS, HFIR)

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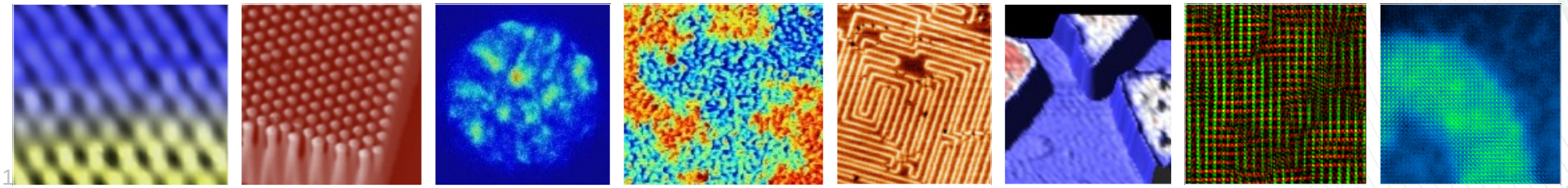
### Research areas:

- **Synthesis** – Soft matter (precision synthesis, selective deuteration), 2D materials, hybrid structures, epitaxial oxides
- **Nanofabrication** – Direct-write (3D) fabrication, e-beam lithography, multiscale fluidics, 10,000 sq. ft. cleanroom
- **Advanced Microscopy** – AFM, STM, aberration-corrected and *in situ* TEM/STEM, He-ion microscopy, atom-probe tomography
- **Chemical Imaging** – Multiple approaches based on mass spectrometry or optical spectroscopies
- **Functional Characterization** – Laser spectroscopy, transport, magnetism, electromechanical phenomena
- **Theory/Modeling, Data Analytics** – Including interactions and co-development with leadership-class, high-performance computing
- **Gateway to Neutron Sciences** – deuterated materials, sample environments, multimodal measurements



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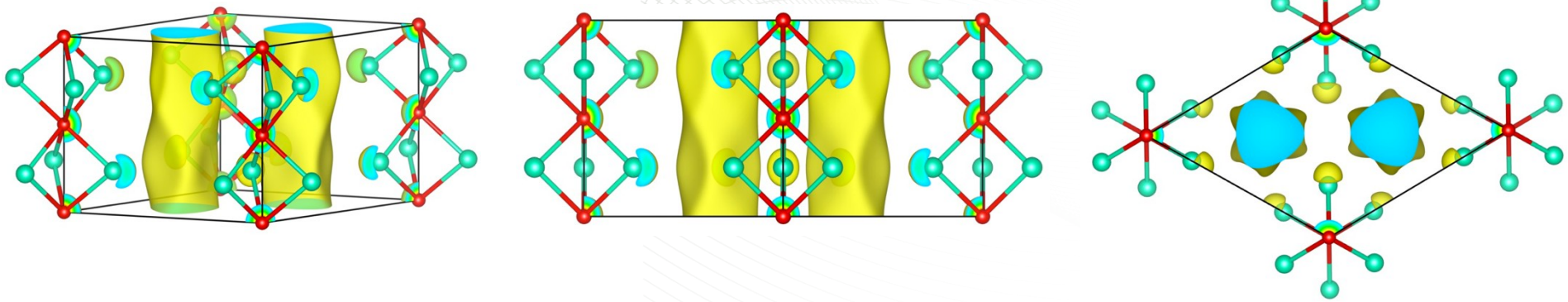
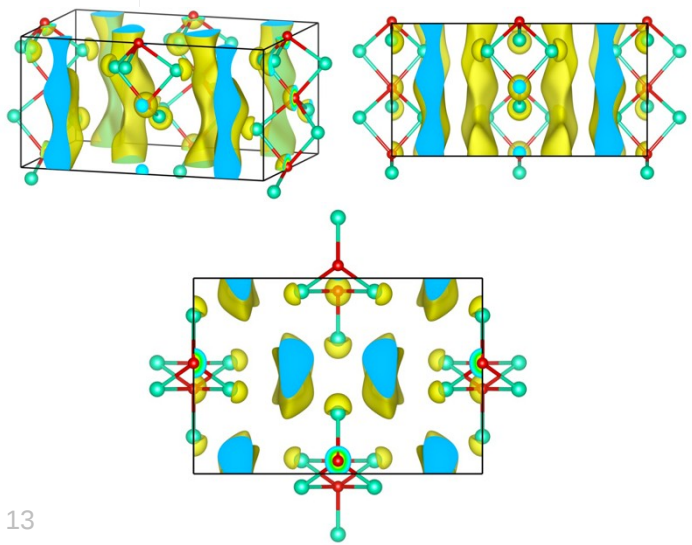
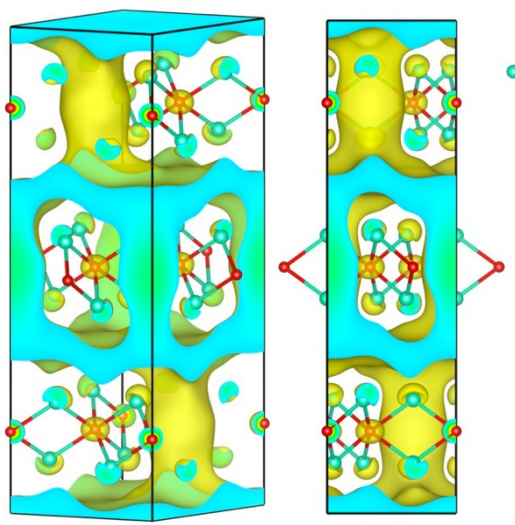
$P6_3/mcm$ (193)



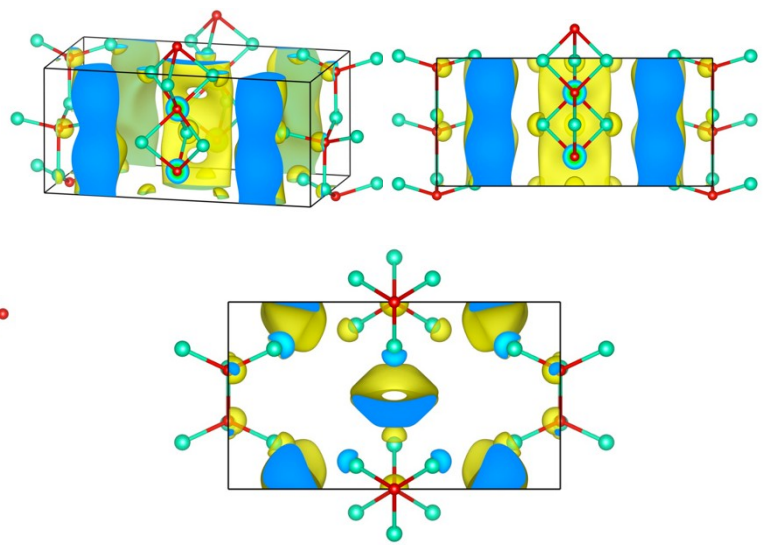
$Cmc2_1$ (36)



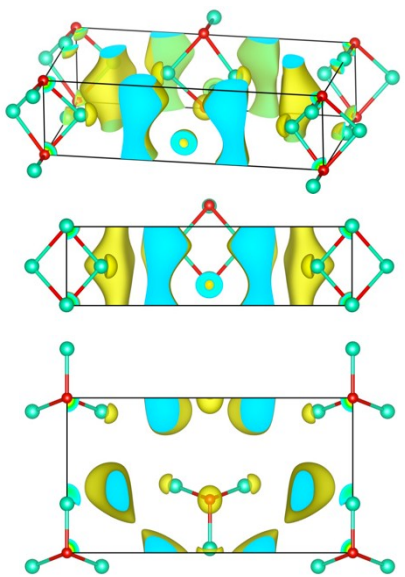
R-3 (148)



$Pmc2_1$ (26)



$P2_1/m$ (11)



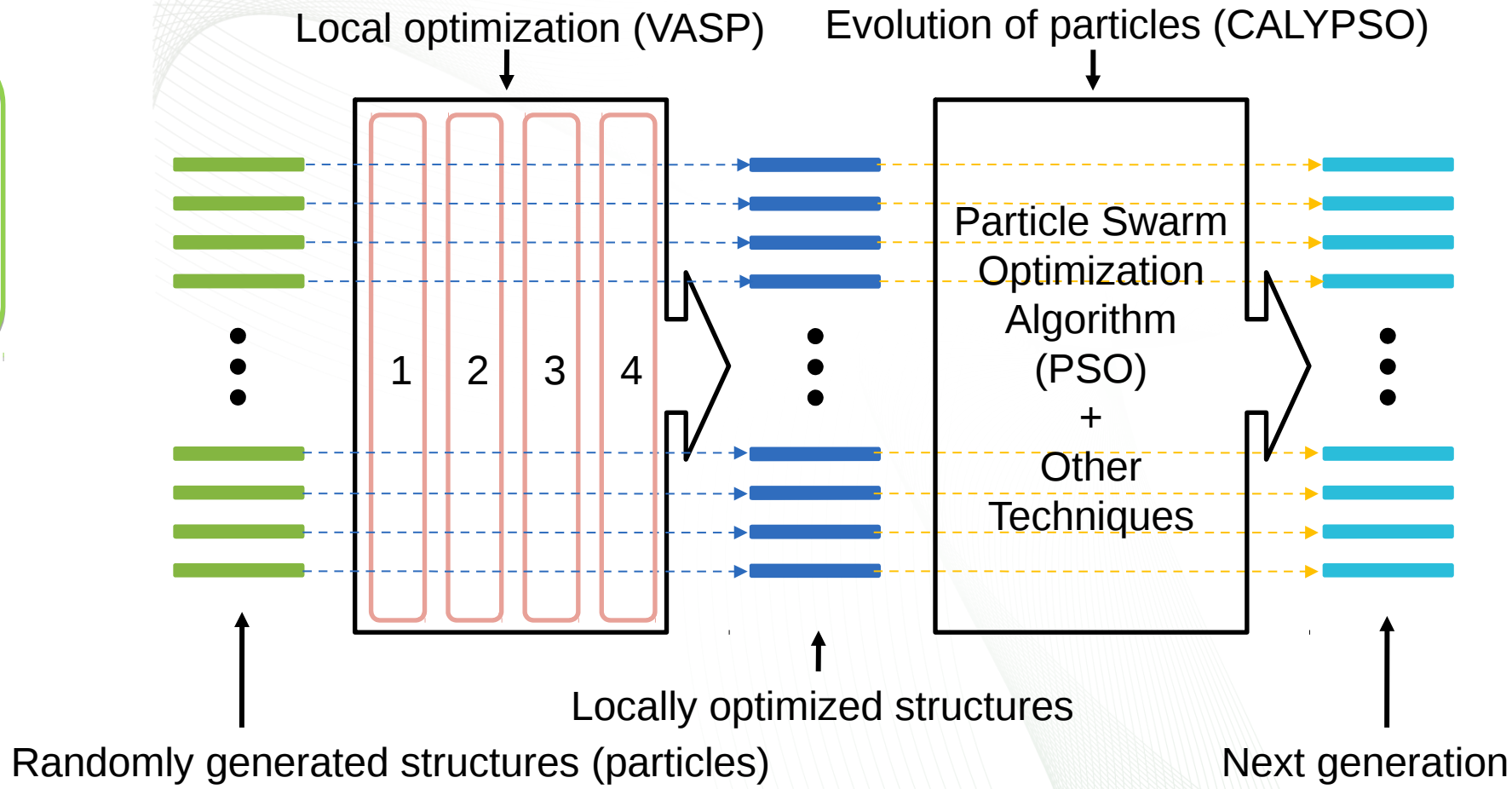
# Computational approach

**Crystal structure**

Particle swarm optimization algorithm (PSO)

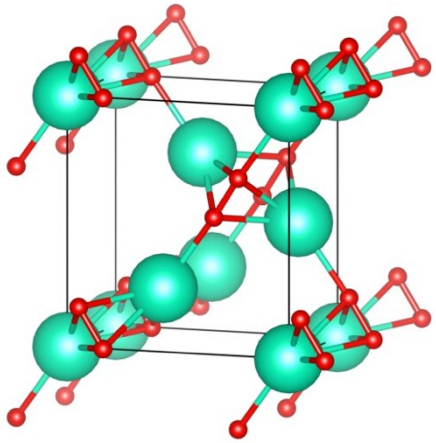
**Electonic structure**

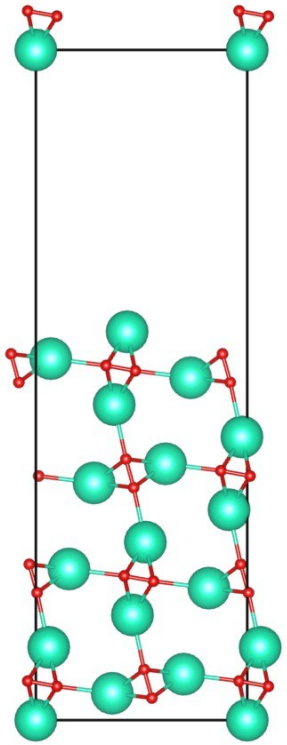
Density functional Theory (DFT)



# **CsO** : stable structures

14(P2_1/c)





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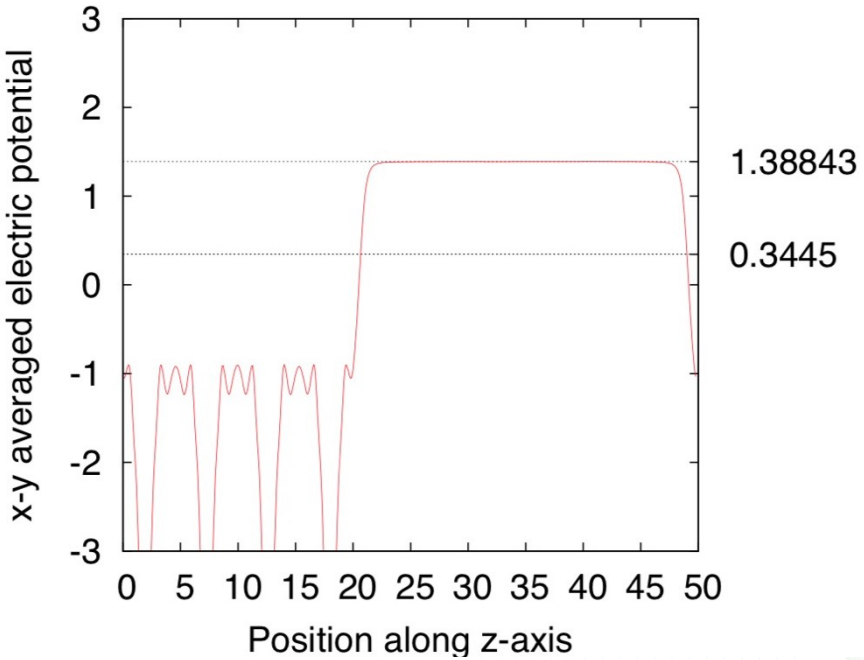
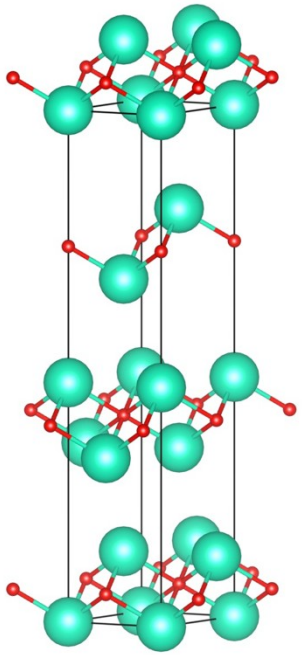
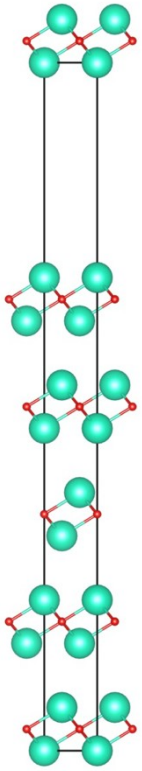



Work function: 1.07026 eV

# $Cs_2O$ : (meta)stable structures

166(R-3m)





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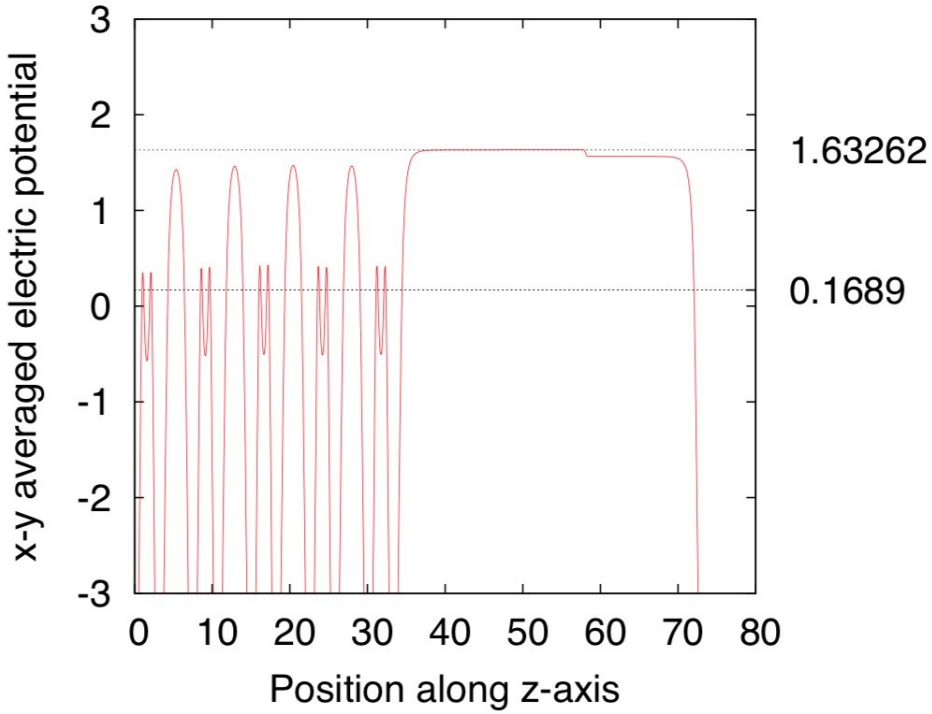


Work function: 1.46748 eV