First-principles exploration of thermodynamically stable Cs–O compounds

Jinseon Park\textsuperscript{1}, Lizhi Zhang\textsuperscript{1}, Mina Yoon\textsuperscript{1,2}

\textsuperscript{1}Department of Physics and Astronomy, University of Tennessee, Knoxville, TN 37916, U.S.A.

\textsuperscript{2}Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, U.S.A.

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

Different oxides are introduced.
Exact composition was not provided.

A: Cs \[\square\] Cs_{11}O_{3}
B: Cs_{11}O_{3} \[\square\] Cs_{2}O_{2}
C: Cs_{2}O_{2} \[\square\] CsO_{2}

Application

• Recent applications as a low work function coating
  - Improvement in thermionic emission in thermionic energy convertor

<table>
<thead>
<tr>
<th></th>
<th>$\phi_{PE}$ (eV)</th>
<th>$\phi_{TE}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K/O:Si</td>
<td>1.73 ± 0.16</td>
<td>1.75 ± 0.28</td>
</tr>
<tr>
<td>Cs/O:Si</td>
<td>1.66 ± 0.27</td>
<td>1.72 ± 0.20</td>
</tr>
</tbody>
</table>

* work function of Silicon : 4.85 eV

- Improvement in electron injection in solar cells


V. Giorgis, et al., J. Appl. Phys. 120, 205108 (2016)
Discovery of a new class of 1D electrides with nontrivial band topology: Cs$_3$O

- **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$_3$O and Ba$_3$N) is the first electrides with nontrivial band topology presenting band inversion and topologically protected quantum states.
- Experimental synthesis is a challenge.


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: Cs₃O, Cs₂O, CsO
  - Electronic structure analysis
  - Work function calculations


Computationally identified metastable configurations

\[
\Delta E_f = \frac{x E(Cs)_{bcc} + y E(O_2)}{2} (x + y)
\]

- 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$_3$O

- New 1D based electride (P6$_3$/mcm)
- metals
- New 1D / 2D structures were identified.

Crystal structures and electronic properties: Cs$_2$O

<table>
<thead>
<tr>
<th>Composition</th>
<th>Formation energy (eV)</th>
<th>Space group</th>
<th>Direct gap (eV)</th>
<th>Global gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$_2$O</td>
<td>-0.925</td>
<td>Pnnm (58)</td>
<td>0.85</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-0.951</td>
<td>Pmmn (59)</td>
<td>0.33</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-0.988</td>
<td>Fd-3m (227)</td>
<td>0.67</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-0.992</td>
<td>Cm (8)</td>
<td>0.96</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>-0.992</td>
<td>R-3m (166)</td>
<td>0.97</td>
<td>0.52</td>
</tr>
</tbody>
</table>

- Cs$_3$O $\rightarrow$ Cs$_2$O: opening of band gaps (<1eV, PBE)
- High band dispersion of conduction bands governed by metallic Cs states
- 2D layered structures were identified.
Crystal structures and electronic properties: CsO

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</tr>
</thead>
<tbody>
<tr>
<td>CsO</td>
<td>-0.939</td>
<td>Amm2 (38)</td>
<td>1.21</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>-1.017</td>
<td>P2₁/c (14)</td>
<td>1.92</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-1.019</td>
<td>Immm (71)</td>
<td>1.71</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>-1.021</td>
<td>C2/m (12)</td>
<td>1.71</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-1.031</td>
<td>P2₁/c (14)</td>
<td>1.02</td>
<td>-</td>
</tr>
</tbody>
</table>

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

- Cs$_2$O 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.
Summary

• Metastable structures of cesium oxides compounds (Cs$_3$O, Cs$_2$O, CsO) were predicted and characterized by using PSO and DFT.

• Cs$_3$O 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
A DOE User Facility for Creating, Characterizing, and Understanding Nanomaterials

Providing free access to staff expertise and equipment if intent is to publish results.

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

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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Computational approach

Crystal structure

Particle swarm optimization algorithm (PSO)

Electronic structure

Density functional Theory (DFT)

Randomly generated structures (particles)

Locally optimized structures

Next generation

Local optimization (VASP) → Evolution of particles (CALYPSO)

Particle Swarm Optimization Algorithm (PSO) + Other Techniques
CsO : stable structures

Work function: 1.07026 eV
Cs$_2$O: (meta)stable structures

166(R-3m)

(0 0 1)

Work function: 1.46748 eV