DFT study of $\text{La}_2\text{Ce}_2\text{O}_7$: A question of order

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BCerS
Mons, February 7th, 2011

Introduction

La$_2$Ce$_2$O$_7$: pyrochlore or disordered fluorite?

Atomistic modeling!

DFT calculations
$\rightarrow$ heat of formation
$\rightarrow$ O-vacancy stability

X-Ray Diffraction
$\rightarrow$ Compare experiment to simulated spectra

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BCerS 2011
Ghent University
From \( \text{CeO}_2 \) to \( \text{La}_2\text{Ce}_2\text{O}_7 \)

\( \text{CeO}_2 \):
- \( \rightarrow \) cubic fluorite lattice
  - 4 Ce sites
  - 8 O sites

\( \text{CeO}_2 \rightarrow \text{La}_2\text{Ce}_2\text{O}_7 \)
- Replace 50% Ce with La
- Remove 1/8 of the O atoms

In the cubic unit cell 3 inequivalent solutions are possible

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Randomly replace 50% Ce by La
Randomly remove 1/8 of O
Specific positions of La & Ce
O-vacancies surrounded by Ce tetrahedron
Cation Positions

Ordered structures

CuAu L1₀
Alternating planes along [001]

L111
Alternating planes along [111]

LZO
Pyrochlore

Cation Positions II

Disordered structure

Special Quasi-random Structure (SQS)

A. Zunger et al. PRL 65, 353 (1990)
C. Jiang et al. PRB 79, 104203 (2009)
O-Vacancy Positions

For each Cation structure:

- All possible-inequivalent positions
- Same chemical surrounding in 1 system
- Notation:
  - NV → No Vacancies (La₂Ce₂O₈)
  - xCeₙLa → Tetrahedron surrounding the O-vacancy consists of x Ce + y La atoms. (x+y=4)

Results: Formation Energy

Without Vacancies: Disordered Fluorite
With Vacancies: Pyrochlore
## Results: Formation Energy

<table>
<thead>
<tr>
<th></th>
<th>PBE</th>
<th></th>
<th>PBE+U</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\Delta H_f) (eV)</td>
<td>(E_{af}) (eV)</td>
<td>(\Delta H_f) (eV)</td>
<td>(E_{af}) (eV)</td>
</tr>
<tr>
<td>c111 Li(_0) NV</td>
<td>1.177</td>
<td>-</td>
<td>1.280</td>
<td>-</td>
</tr>
<tr>
<td>c111 Li(_0) 2Ce2La</td>
<td>0.758</td>
<td>-0.419</td>
<td>0.800</td>
<td>-0.480</td>
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<tr>
<td>LZO NV</td>
<td>1.167</td>
<td>-</td>
<td>1.364</td>
<td>-</td>
</tr>
<tr>
<td>LZO 2Ce2La</td>
<td>0.939</td>
<td>-0.220</td>
<td>1.105</td>
<td>-0.259</td>
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<tr>
<td>LZO 4Ce</td>
<td>-0.016</td>
<td>-1.183</td>
<td>0.220</td>
<td>-1.143</td>
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<tr>
<td>LZO 4La</td>
<td>1.668</td>
<td>0.501</td>
<td>1.620</td>
<td>0.256</td>
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<tr>
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<td>1.564</td>
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<tr>
<td>L111 3Ce1La</td>
<td>0.452</td>
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<tr>
<td>L111 1Ce3La</td>
<td>1.359</td>
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<tr>
<td>SQS NV</td>
<td>1.160</td>
<td>-</td>
<td>0.699</td>
<td>-</td>
</tr>
<tr>
<td>SQS Vac</td>
<td>0.527</td>
<td>-0.633</td>
<td>0.607</td>
<td>-0.91</td>
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0 Ce \(\rightarrow\) 1 Ce \(\rightarrow\) 2 Ce \(\rightarrow\) 3 Ce \(\rightarrow\) 4 Ce

PBE: +0.50 eV \(\rightarrow\) +0.18 eV \(\rightarrow\) -0.32 eV \(\rightarrow\) -0.72 eV \(\rightarrow\) -1.18 eV

Ce surrounding \(\rightarrow\) stabilizes O- vacancy

## Results: Lattice Expansion

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<thead>
<tr>
<th></th>
<th>(V) (%)</th>
<th>(a) (Å)</th>
<th>(\Delta a) vs CeO(_2) (%)</th>
<th>(\Delta a) vs NoVac (%)</th>
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<tr>
<td>c111 Li(_0) NV</td>
<td>7.945</td>
<td>5.699</td>
<td>2.281</td>
<td>-</td>
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<tr>
<td>c111 Li(_0) 2Ce2La</td>
<td>-1.031</td>
<td>5.579</td>
<td>2.021</td>
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<td>LZO NV</td>
<td>8.479</td>
<td>5.618</td>
<td>2.750</td>
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<tr>
<td>LZO 2Ce2La</td>
<td>-1.533</td>
<td>5.590</td>
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<tr>
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<td>-0.228</td>
<td>5.614</td>
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<tr>
<td>LZO 4La</td>
<td>-3.793</td>
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<td>L111 3Ce1La</td>
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<tr>
<td>L111 1Ce3La</td>
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<td>2.526</td>
<td>-0.430</td>
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PBE+U: +1.4% \(\rightarrow\) +1.8% \(\rightarrow\) +2.1% \(\rightarrow\) +2.4% \(\rightarrow\) +2.7%

Ce surrounding \(\rightarrow\) Lattice Expansion
Results: Lattice Expansion

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PBE+U:

Ce surrounding → Lattice Expansion

Experiments:

+2.0%  

+2.79%  

Results: X-Ray Diffraction

Contains 9 Fluorite peaks

Expected pyrochlore peaks:
(311), (331) & (511)

Low intensity <1%
Results: X-Ray Diffraction

Low intensity

Peak splitting

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Results: X-Ray Diffraction

- No splitting and reasonable intensities
- Pyrochlore peaks

+ No peak splitting
- Too low intensity high angle peaks
**Results: X-Ray Diffraction**

![X-Ray Diffraction Graph](image)

- **Pyrochlore**
  - no peak splitting
  - pyrochlore peaks (<0.5% intensity)
  - relative peak intensities

- **Disordered Fluorite**
  - no peak splitting
  - no pyrochlore peaks
  - relative peak intensities

**Conclusions**

- O-vacancies play a crucial role w.r.t. stability
- Ce in the vacancy surrounding tetrahedron increases stability
- Ce-tetrahedra are most stable
- Favors ordered over disordered structures

- X-Ray Diffraction can distinguish different structures
  - Multiple peak-splittings for many structures
  - Pyrochlore and Disordered Fluorite show no peak splitting
  - Pyrochlore shows best relative intensities

**La$_2$Ce$_2$O$_7$:** Disordered Fluorite vs Pyrochlore