Density-Functional Study of the $\text{La}_2\text{Zr}_2\text{O}_7$ Low-Face Indexes

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Introduction

- Lanthanum zirconate (La$_2$Zr$_2$O$_7$, LZ) and doped forms of LZ have been shown to be effective catalysts.
- Doped forms of LZ can catalyze reactions to make syngas (CO + H$_2$), used as a fuel in solid oxide fuel cells (SOFCs), to make various chemicals.
- Partial oxidation of fuel to syngas$^1$: 2CO + $n$H$_2$O $\rightarrow$ 2CO$_2$ + $n$H$_2$ + $m$H$_2$O
- Dry reforming of methane: 3CH$_4$ + CO$_2$ $\rightarrow$ 4CO + 6H$_2$
- Oxidation of methane (close deactivation)$^2$: 3CH$_4$ + CO$_2$ + $n$O$_2$ + $m$H$_2$O $\rightarrow$ 4CO + 8H$_2$ + $n$O$_2$ + $m$H$_2$O
- LZ and doped forms can catalyze C$_x$H$_y$ combustion$^3$: CH$_x$ + 2O$_2$ $\rightarrow$ CO$_2$ + $x$H$_2$O

$\text{La}_2\text{Zr}_2\text{O}_7$-based compounds have also been studied to catalyze other processes: Higher alcohols synthesis by CO hydrogenation$^4$

To explain the effectiveness of LZ and doped form of LZ as catalysts, an understanding of LZ surfaces is needed.

From previous experimental work, the structure of bulk LZ is pyrochlore, with four different atom types (Z = La$_2$Zr$_2$O$_7$). The low-index surfaces, (001), (011), and (111), are likely to be well represented.$^{5,6}$

Recently, the first theoretical study of LZ surfaces was published$^{14}$: An ideal surface is defined as a surface with a termination surface or top atomic layer or layers that can be formed by cleaving the bulk crystal.

By computing surface free energies of different surface terminations at the level of density-functional theory (DFT), evidence is provided that the (001) surface is nonideal over a large set of experimental conditions.

Building on ref 14, the main goal of this work is to provide evidence that all possible ideal surface terminations of the (001), (011), and (111) surfaces are nonideal.

Computational Approach

- Results are obtained at the level of DFT using, unless otherwise noted:
  - PwW95 functional
  - Plane-wave basis set with 400 eV cutoff
  - PwW95 pseudopotential set
  - Monolayer-Pack-A point meshes for bulk materials and surfaces (e.g., 4 x 4 x 4 for bulk and 4 x 4 x 1 for surface)
- Surfaces are modeled using the slab technique and a slab model plus 16 Å vacuum region.

Surfaces of LZ

- All possible ideal surface terminations of the (001), (011), and (111) surfaces are examined. They are labeled (001) 1-10, (011) 1-12, and (111) 1-18.
- Ideal surface terminations of LZ (001), (011), and (111), ideal surfaces, described by specifying the top atomic layer for the smallest possible surface unit cell. For surface terminations that are identical, the underlying layer is given in a footnote.

Preferred (001), (011), and (111) Surface Termination versus $\Delta\mu_{0}$

The surface free energy $\mu_0$ is the energy to form a surface from the bulk crystal taking into account environmental conditions:

$$\Delta\mu_0 = \frac{1}{2} \left[ G^\text{ad} (F, \rho_0) - G^\text{ad} (F', \rho_0') + k\text{ln} \rho_0' - \rho_0 \right]$$

$G^\text{ad}$: Gibb's free energy of O$_2$ at T and $\rho_0$; $F' = 388.15$ K, $\rho_0' = 1$ atm

$G^\text{ad}$: energies per bulk mole of $\text{La}_2\text{O}_3$ + La$_2$O$_3$ and Zr$_2$O$_3$ + M = La + Zr, respectively (from DFT)

$\Delta\mu_{0}$: experimental standard heat of formation of LZ

$\Delta\mu_{0}$: experimental standard entropy of O$_2$

The preferred (001), (011), and (111) surface termination versus T and $\log (\rho_0/1$ atm) is shown on the right (top, middle, and bottom plots, respectively). Above 1200 K, results can only be estimated due to the breakdown of the SHA or standard harmonic approximation, as discussed in the next section.

Validation and Implications of Results

- Vibrational contributions to the functions $\Omega$ and in determining potential lines (left, bottom) may be important. They are taken into account by computing phonon densities of states to make new diagrams (right), similar to the original diagrams.
- The SHA made to determine vibrational contributions is expected to break down above roughly half of bulk LZ's melting point. Thus, the original diagrams cannot be verified above 1200 K.
- Diagrams are also obtained within the local density approximation (shown), similar to the original diagrams.

Comparison to Experiment

- Using $\Omega$ values of preferred ideal (001), (011), and (111) surface terminations, Wulff shapes, or crystal shapes having minimal $\Omega$, are made at LZ synthesis conditions of 0.2 atm O$_2$ and 513, 1173, and 1473 K (right). At every T, a set of shapes is obtained, because $\Omega$ of the preferred ideal (111) surface termination will span a range of values.
- If the experimental shape made at 0.2 atm O$_2$ and a T given above is different from the shape of the experimental shape may be nonideal. Before this comparison can be made, the experimental shapes need to be determined.

Conclusions

- In this work, the (001), (011), and (111) surfaces of LZ are studied theoretically, complementing a previous theoretical study.$^{16}$
- Only certain surface terminations of a given surface are preferred.
- Evidence is provided for a nonideal (001), (011), and (111) surface under large sets of conditions of T and $\rho_0$.
- The above two conclusions are not affected by vibrational effects.
- A comparison to experiment is proposed.

Acknowledgment

- SOFC Program at the National Energy Technology Laboratory

References