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BaZrO3 Perovskite for Solar Thermal Water Splitting Applications: High Temperature Redox Thermochemistry

K. K. Ghose,[a] A. Bayon,[b] and A. J. Page[a,*]
[a] Priority Research Centre for Frontier Energy Technologies and Utilisation, The University of Newcastle, Callaghan, 2308, Australia.
[b] CSIRO Energy Technology, Newcastle, 2304, Australia.

1. Introduction

ABO_3 perovskites are attractive candidates for sustainable energy conversion processes such as solar thermochemical water splitting (STWS), solid oxide fuel cells (SOFC) and photocatalysis due to their ability to produce mixed oxidation states.[1] In two steps STWS redox cycle, the performance of ABO_3 as redox materials is dominated by their free energy associated with the formation or removal of oxygen vacancies in the reduction and oxidation reactions, respectively. Here, we examine the redox thermochemistry of stoichiometric and non-stoichiometric $BaZrO_{3-\delta}$ (δ = 0 – 0.5) perovskite under conditions relevant to STWS using first principles density functional theory (DFT) and density functional perturbation theory (DFPT) calculations. The optimum oxygen non-stoichiometry in $BaZrO_{3-\delta}$ for most favorable STWS is found δ ~ 0.26-0.36 at standard conditions. However, the change in Gibbs free energy for the reduction reaction of $BaZrO_{3-\delta}$ never reach negative values at high temperature up to 2500 K to be viable for thermodynamically favorable spontaneous reaction in STWS redox cycle.

2. Methods

An accurate density functional theory (DFT) protocol for modelling the electronic structure of $BaZrO_3$ is established and applied it to the calculation of phonon dispersion and thermochemical properties using VASP[2] and PHONOPY[3] package, which in turn are used to predict their oxygen vacancy formation energy. Spin-polarized DFT calculations are performed with the PBE exchange-correlation functional and PAW pseudo-potentials, see Figure 1.

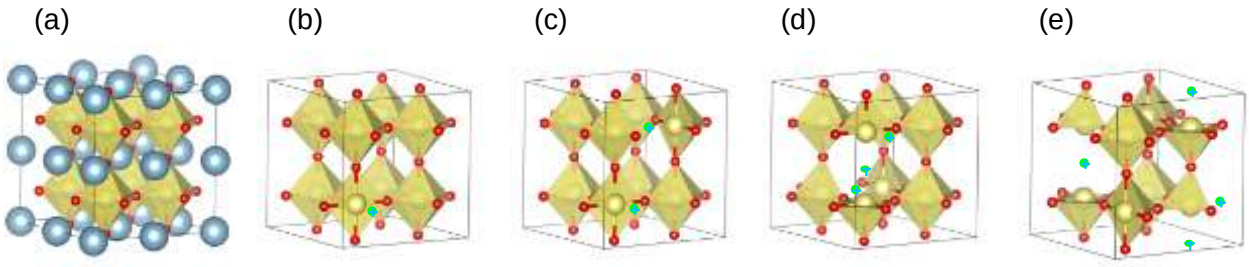

Figure 1. 2×2×2 supercells of (a) pristine $BaZrO_3$ (b) $BaZrO_{2.875}$ (c) $BaZrO_{2.75}$ (d) $BaZrO_{2.625}$ (e) $BaZrO_{2.5}$. Grey, gold and red spheres represent Ba, Zr and O atoms, respectively. (b)-(e) omit Ba for clarity. Green spheres represent position of oxygen vacancy defect in (b)-(e). Gold surfaces indicate ZrO_3 octahedra.

3. Results & Discussion

The optimum oxygen non-stoichiometry in $BaZrO_{3-\delta}$ for most favorable STWS is found in δ ~ 0.17-0.23 at standard conditions according to the suggested literature.[4] Figure 2(a) presents the results for the

vacancy formation energies of pristine $BaZrO_3$ and defective $BaZrO_{3-\delta}$ as a function of defect stoichiometry.

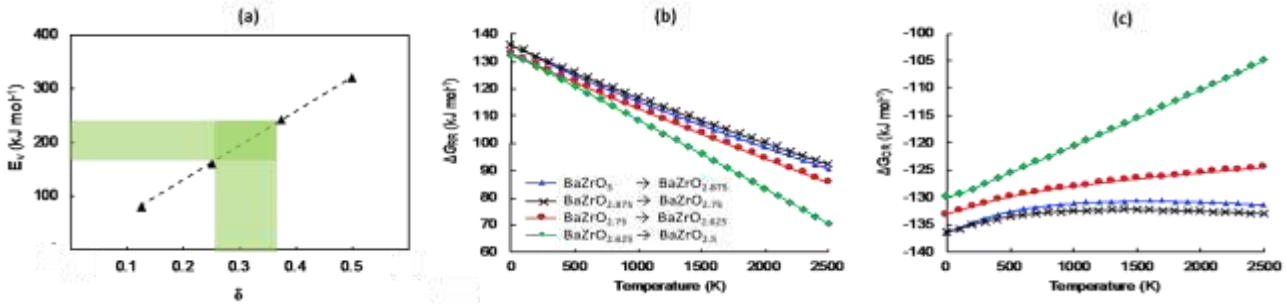

Figure 2. (a) PBE-PAW E_v values (per defect) of $BaZrO_{3-\delta}$ as a function of oxygen non-stoichiometry δ. The green region indicates the optimum E_v range of 170 – 230 kJ mol^{-1} (1.8-2.4 eV).[4] The change in Gibbs free energy of **(b)** reduction reaction, $\Delta G_{\mathrm{RR}}(T,p)$ (equation (6) and **(c)** oxidation reaction, $\Delta G_{\mathrm{OR}}(T,p)$(equation (7).

However, with the increase of temperature the change in Gibbs free energy for the reduction reaction $\Delta G_{RR}[T,p]$ of $BaZrO_{3-\delta}$ never reach negative values upto 2500 K. At 2500 K the average $\Delta G_{RR}[T,p]$ values of four reduced state - $BaZrO_{2.875}$, $BaZrO_{2.75}$, $BaZrO_{2.625}$, and $BaZrO_{2.5}$ have been found 90.54,92.27, 85.62 and 70.29 kJ mol^{-1} respectively (Figure-2(b)). Figure 2(c) shows consecutive oxidation state of $BaZrO_{2.875}$, $BaZrO_{2.75}$, $BaZrO_{2.625}$, $BaZrO_{2.5}$ against the temperature range 0-2500 K. The deviation of vacancy formation energies between each reduced state comes from the entropic and enthalpic contribution of corresponding reduced state. The increase in internal energy of the entire system at high temperature cause disorder in the crystal structure. Furthermore, with the increase of vacancy concentration the change of crystal phase, effect on thermodynamic properties, and hence lower the entropy, specific heat.

4. Conclusions

From the redox properties of $BaZrO_{3-\delta}$, the optimum energetically favorable $\Delta G_f[Vo]$ can be obtained at standard conditions, however, at high temperature, $\Delta G_f[Vo]$ never reached negative values for spontaneous reduction reaction upto 2500 K. This result indicates that, a metal oxide fall in STWS favorable range at standard conditions doesn't necessarily mean that, they will remain favorable at high temperature for STWS cycle. The assumed negligible vibrational contributions by Delm et al.[4] in calculation of E_v at standard conditions, become significant at high temperature which make difference in the change of Gibbs free energy as it observed for $BaZrO_{2.5}$ in reduction and oxidation reaction. This study reveals that high temperature screening of defect perovskites are significant to elucidate the potentiality of a such materials for STWS.

References

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