

Electronic Structure and High-Temperature Thermochemistry of BaZrO_{3-δ} Perovskite from First-Principles Calculations

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Abstract

ABO_{3-δ} perovskites are attractive candidates for high-temperature mixed ionic electronic conduction processes, due to their ability to produce mixed oxidation states and accommodate oxygen vacancies. Here, we examine the electronic structure and high-temperature thermochemistry of stoichiometric and non-stoichiometric cubic BaZrO_{3-δ} perovskites for high defect concentration ($d = 0-0.5$) using first principles density functional theory (DFT) and density functional perturbation theory (DFPT) calculations. Our results show that the electronic structures of these perovskites under increasing oxygen deficiency are characterized by highly localized reduction of Zr⁴⁺ t_{2g} orbitals in the vicinity of the oxygen defects, irrespective of the value of d . Temperature dependent thermodynamic properties of pristine- and defective-BaZrO_{3-δ} show consistency with oxygen vacancy concentration. A comparison of predicted thermochemical properties with and without explicit vibrational corrections demonstrates their relative stability and implications at high-temperatures, as reduction Gibbs free energies in BaZrO_{3-δ} exhibit large deviations above 1000 K. We elucidate the physical origins of these deviations via a phonon mode analysis.

Results

As an example of results, calculated vibrational S , C_p and $[H^\circ(T)-H^\circ(298.15\text{ K})]$ values for the $2 \times 2 \times 2$ supercell of pristine- and defective-BZO_{3-δ} ($\delta = 0-0.5$) between 0–2000 K are shown in Fig. 1 (a–c). Fig. 1(a) shows that, at an equivalent temperature, S is inversely proportional to the extent of reduction to the BZO lattice (i.e. higher d), as anticipated (since fewer atoms in the supercell will yield a lower entropy). Nevertheless, the change in S with d becomes larger at high-temperature. For instance, as d increases from 0 to 0.5, S drops from 1057 to 1000 J K⁻¹ mol⁻¹ at room temperature (a change of -57 J K⁻¹ mol⁻¹), whereas it drops from 2874 to 2617 J K⁻¹ mol⁻¹ at 2000 K (a change of -257 J K⁻¹ mol⁻¹). Similar trends are observed for constant pressure heat capacities of BZO_{3-δ}, shown in Fig. 1(b). In general terms, these heat capacities vary as one would expect; at low temperatures C_p obeys Debye's T^3 law, while over 500 K, C_p deviates from the classical limit of Dulong–Petit's law due to lattice contributions from anharmonicity and quasi-harmonicity, consistent with data reported for pristine BZO. Nevertheless, the variation in C_p with increasing d is larger at high-temperature than at standard conditions. For instance, at 2000 K, C_p drops by 113 J K⁻¹ mol⁻¹ for $\delta = 0.5$, whereas this change is only 83 J K⁻¹ mol⁻¹ at room temperature.

Conclusions

We have presented first-principles simulations predicting the electronic structure and high-temperature thermochemical properties of highly defective non-stoichiometric BZO_{3-δ} ($\delta = 0-0.5$) perovskites. DFT calculations demonstrate that reduction of the BZO lattice in the presence of neutral oxygen vacancy defects is highly localized on neighbouring Zr⁴⁺ t_{2g} orbitals, irrespective of the value of δ . Thermodynamic properties of BZO such as entropy, specific heat, molar enthalpy at

low- and high-temperature show excellent agreement with experimental data. On this basis, thermodynamic properties of nonstoichiometric $\text{BZO}_{3-\delta}$ perovskite are reported here between 0–2000 K and demonstrate that how thermochemical properties of $\text{BZO}_{3-\delta}$ are both temperature and oxygen vacancy dependent. Analysis of vacancy formation energies demonstrated the vacancy dependent stability of $\text{BZO}_{3-\delta}$ at high defect concentration, and for this perovskite vibrational contributions are significant at high-temperature, which lead to marked deviation in reduction free energies above 1000 K. We have elucidated the origin of these deviations via DFPT phonon analysis, noting that increased oxygen deficiency in the BZO lattice leads to larger amplitude ZrO_3^{2-} breathing vibrations and a non-linear relationship between δ and the high frequency O^{2-} vibrations in the $\text{BZO}_{3-\delta}$ lattice. The effect of oxygen partial pressure on reduction temperature of $\text{BZO}_{3-\delta}$ established their reducibility and applicability at low pressure.

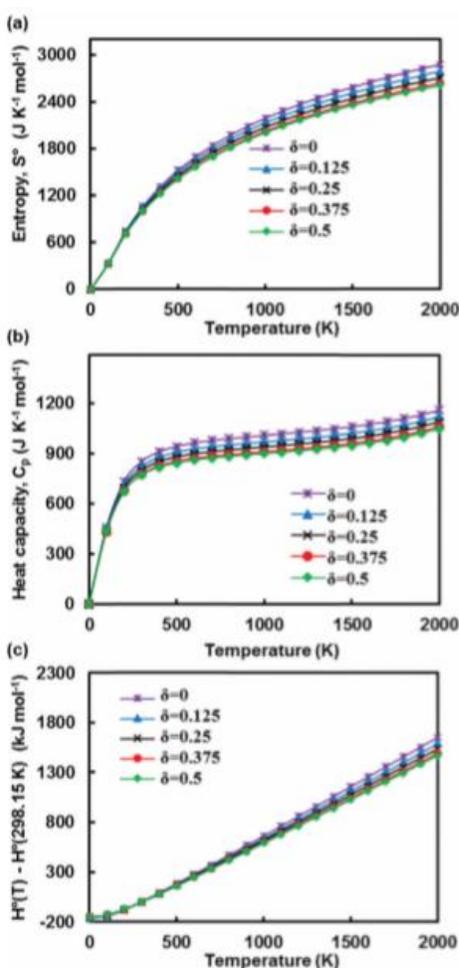


Figure 1: Calculated PBE-PAW (a) entropy, S ($\text{J K}^{-1} \text{mol}^{-1}$), (b) specific heat at constant-pressure, C_p ($\text{J K}^{-1} \text{mol}^{-1}$), and (c) relative molar enthalpies, $[H^{\circ}(T) - H^{\circ}(298.15 \text{ K})]$ (kJ mol^{-1}) of pristine- and defective- $\text{BZO}_{3-\delta}$ ($\delta = 0-0.5$) between 0–2000 K temperatures using a $2 \times 2 \times 2$ supercell (Ghose et al.).

Reference

K.K. Ghose, A. Bayon, J. Hinkley and A. J. Page, Electronic structure and high-temperature thermochemistry of $\text{BaZrO}_{3-\delta}$ perovskite from first-principles calculations. *Phys. Chem. Chem. Phys.* 2019, 21, 12468-12476.