

Electronic Supporting information (ESI)

Thermochemical Properties of Rare-Earth Oxyhydrides From First Principles Phonon Calculations

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1. Computational details

All calculations were performed using first principles within Density Functional Theory (DFT) as implemented in the VASP code.^{1,2} We applied the GGA-PBE exchange correlation functional³ and the core potentials were treated by the projector augmented-wave (PAW) method.⁴ For Ca, O and H, we used potentials with Ca_sv, O and H, while for La, Ce, Pr, Nd, Gd and Er we used potentials with La, Ce_3, Pr_3, Nd_3, Gd_3, and Er_3. The electronic wave functions were expanded using a set of plane waves with a constant plane-wave cut-off of 600 eV. All total energies were converged with respect to the k-point density. Structural optimizations were performed by allowing full lattice and volume relaxations to within residual forces of 10^{-4} eV/Å, while the electronic structure was optimized to within 10^{-8} eV for self-consistency.

The phonon frequencies at constant volume were obtained within the harmonic approximation using finite ionic displacements of ± 0.01 Å with $2 \times 2 \times 2$ supercell expansions for rare-earth oxyhydrides, rare-earth metals and Ca compound (CaH₂ and CaO), while $1 \times 1 \times 1$ cells were used for rare-earth oxides due to the large cell parameters (more than 10 Å). The electronic structure of all distorted supercells was converged to within 10^{-8} eV, and the resulting Hellmann-Feynman forces acting on all ions were used to build the force constant matrices. The phonon frequencies were subsequently obtained through Fourier transform and diagonalization of the dynamical matrix as implemented in the Phonopy code.⁵ The subsequent diagonalization and Fourier transform, and derivation of thermodynamic properties were also performed with Phonopy). This allowed determination of vibrational contributions – including “zero-point” corrections - to the Helmholtz free energy through;

$$F^{vib} = 0.5 \sum_{q,s} h\nu(q,s) + k_B T \sum_{q,s} \ln \left(1 - \exp \left(- \frac{h\nu(q,s)}{k_B T} \right) \right) \quad (\text{Eq. 1})$$

$$S^{vib} = -k_B \sum_{q,s} \ln \left(1 - \exp \left(- \frac{h\nu(q,s)}{k_B T} \right) \right) + \frac{1}{T} \sum_{q,s} \frac{h\nu(q,s)}{\exp \left(\frac{h\nu(q,s)}{k_B T} \right) - 1} \quad (\text{Eq. 2})$$

where $\nu(q,s)$ was the frequency of mode s throughout q space. Although constant-pressure effects could be accounted for through the quasi-harmonic approximation, these first estimates of the REHO thermochemistry were based on constant volume calculations (i.e. neglecting thermal expansion effects). In order to address potential anharmonic effects, displacements of 0.005 and 0.015 Å were also tested. The deviations observed were within 0.2 kJ/mol, indicating that anharmonic effects could be neglected.

2. Thermodynamic calculations

The Gibbs free energy, G , of the solid phases at finite temperatures can be represented by;

$$G(p,T) = E_0 + H^\circ(T) - TS^\circ(T) \quad (\text{Eq. 3})$$

while those of the gas molecules are taken as;

$$G(p,T) = E_0 + H^\circ(T) - TS^\circ(T) + RT \ln \frac{p}{p^\circ} \quad (\text{Eq. 4})$$

where E_0 are the total electronic energies obtained from first principles calculations. In terms of solid materials, $H^\circ(T) - TS^\circ(T)$ is the vibrational free energy of the lattice ions according to Eq. 1. $H^\circ(T)$ and $S^\circ(T)$ of the gas

phases are taken from tabulated data.⁶ In evaluation of the reaction energies of oxyhydride formation and decompositions, we consider atmospheric conditions corresponding to dry hydrogen gas. Moreover, it should be noted that O₂ binding energy (experimental value, -504.52 kJ/mol) has been corrected for the errors associated with the GGA functional.⁷⁻⁹ The corrected total energy of O₂ is determined from the calculated energy of the single O atoms and experimental O₂ binding energy, shown in the following Equation 5;

$$E_{total} = 2E_O + E_{Exp\ bind} \quad (\text{Eq. 5})$$

The partial pressure of H₂O has been fixed to typical experimental values for dried gases (10⁻⁵ bar), and the partial pressure of H₂ is kept at 10³ bar. p_{O_2} is in turn determined from the equilibrium;



and is thus temperature dependent (Figure S1).

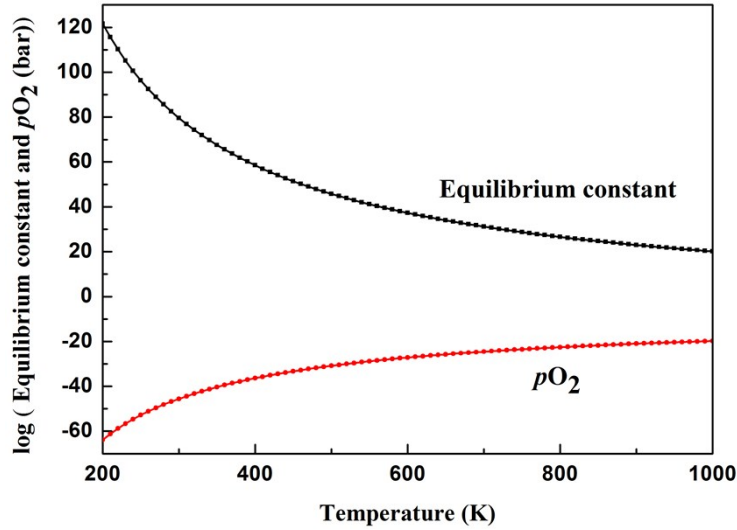


Figure S1. The change of equilibrium constant and partial pressure of O₂ as a function of temperature ($p_{H_2}=10^3$ and $p_{H_2O}=10^{-5}$ bar).

The cohesive energy, E_{coh} , which indicates the stability of crystal structure, may be calculated by the following equation;

$$E_{coh} = \frac{E_0}{Z} - \sum E_{atom} \quad (\text{Eq. 7})$$

where E_0 is the total energy of a unit-cell, Z is the number of molecules per unit-cell, and E_{atom} is the total energy of the isolated atoms. For the different synthesis routes, the cohesive energies of each reaction are calculated as the difference between the cohesive energy of reactants and products;

$$E_{coh, reaction} = \sum E_{coh, reactant} - \sum E_{coh, product} \quad (\text{Eq. 8})$$

3. Structural models

For the REHO, we adopt the structure determined by Widerøe *et al.*¹⁰ for NdHO through powder neutron diffraction and Rietveld refinements ($P4/nmm$ - no. 129 - with $a = a=7.8480(5)$ Å, $c=5.5601(8)$ Å and $z=8$). The

structure exhibits three different hydride/oxide coordination environments around the metal cations (Fig. 1), and resembles fluorite-structured oxides such as ZrO_2 . As the objective of this study is not to investigate H/O order/disorder but to determine trends in the thermochemical properties of the REHO series, we have adopted the ordering reported by Widerøe *et al.*¹⁰ and by Malaman and Brice.¹¹ Further, we adopt the following structures for the remaining phases in Eq 1-3; CaO (Fm-3m),¹² CaH_2 (Pnma),¹³ RE_2O_3 (c-type, Ia-3 structure)¹⁴ and $RE(OH)_3$ (P63/m)¹⁵.

4. RE oxidation free energy and comparison with standard database

Standard thermodynamic data of RE metal oxidation is used to validate our adopted method;



Figure S2 shows the free energy of reaction Eq. 8 as determined from our first principles phonon calculations, compared with experimental values. All the experimental thermodynamic data were taken from the HSC 4.0 software data base.¹⁶⁻²⁶ Figure S2 and Table S1 clearly show that the overall agreement between calculated free energy and the standard data base strongly support the applicability of our first principle phonon calculations within the harmonic approximation. However, there are still some disagreements, which could be caused by both the core potentials used for rare-earth metals, but also inconsistencies in the experimental values stemming from for instance non-equilibrium effects.

Figure S2. (A) The calculated, and (B) experimental standard free energy of RE oxidation according to Eq. 9.

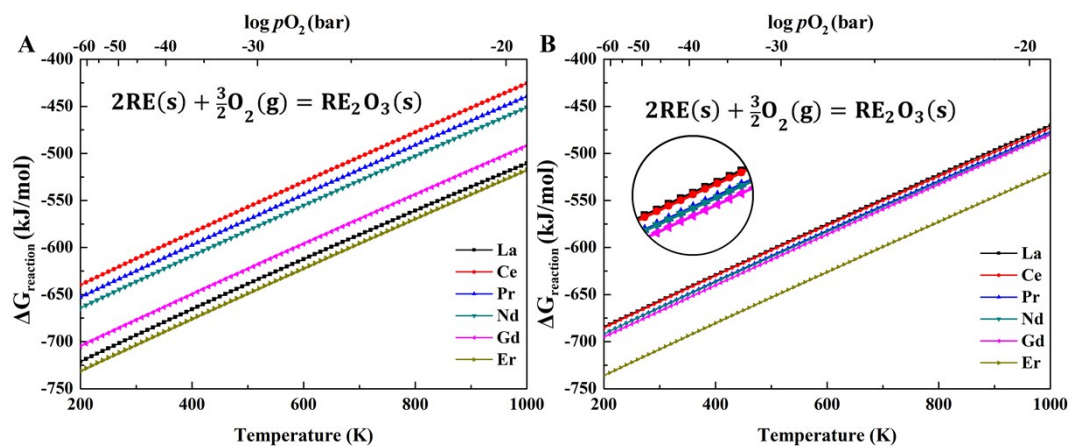


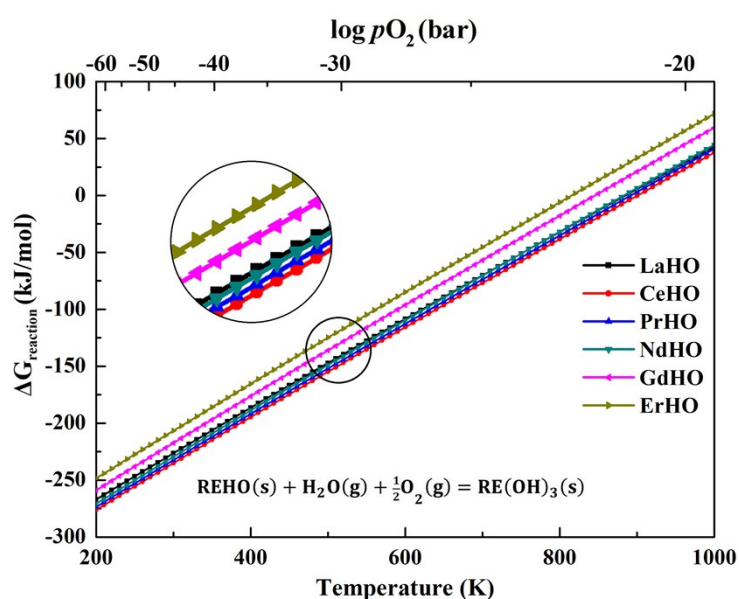
Table S1. Calculated RE metal oxidation free energy (Cal, kJ/mol) and comparison with standard database (Std, kJ/mol).

Temperature		200	400	600	800
LaHO	Cal	-721.30	-665.69	-612.37	-560.86
	Std	-684.25	-629.07	-575.25	-522.40
CeHO	Cal	-639.72	-584.24	-530.35	-477.59
	Std	-685.39	-630.02	-576.52	-524.32
PrHO	Cal	-652.73	-597.46	-543.74	-491.15
	Std	-691.74	-635.97	-581.96	-529.11

NdHO	Cal	-664.07	-608.90	-555.27	-502.76
	Std	-691.67	-636.76	-583.29	-530.81
GdHO	Cal	-704.78	-649.73	-596.13	-543.65
	Std	-695.09	-640.28	-586.17	-532.90
ErHO	Cal	-731.02	-675.83	-622.06	-569.37
	Std	-735.89	-680.29	-625.95	-572.55

5. The Gibbs free energy of REHO decomposition to RE hydroxides.

Figure S3. Gibbs free energy of REHO (RE=La, Ce, Pr, Nd, Gd and Er) decomposition with O₂ and H₂O to form the RE hydroxides (RE(OH)₃) as a function of temperature.



6. Reference

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