Supplementary Information

S1. Computational Methods and Models

Density functional theory (DFT) calculations were performed using the Vienna Ab-initio Simulation Package (VASP) code. A plane wave cutoff energy of 500 eV was used for total energy calculations. The electron-ion interactions were described by using projector augmented wave (PAW) method. The generalized gradient approximation (GGA) was employed with the exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE). The Monkhorst-Pack grid was chosen based on the cell size. The structures were relaxed until total energy change between two steps was smaller than 0.1 meV. The force tolerance of 0.03 eV/Å was used. A vacuum region of 15 Å was adopted to avoid interactions between slabs in the z-direction. TheMonkhorst-Packscheme *k*-points grid sampling was set at 2×2×1 for the optimization of supercell (2 × 2) slabs. In addition, dipole corrections were included in the direction perpendicular to the surface. We used the climbing image nudged elastic band (CI-NEB) method, to find transition states (TS) and confirmed it with frequency calculations. The force tolerance of 0.05 eV/Å was used in this method and images were interpolated linearly between the initial and final state.

The vacancy formation energy required to create an O vacancy is defined following the approach used by Ganduglia-Pirovano et al.:

$$E_f = (E_{def} - E_{free} + N_{def} * E_{O2}/2)/N_{def}$$

Here N_{def}, E_{def} and E_{free} represent the number of oxygen vacancy, the total energy of defect and defect-free systems, respectively. E_{O2} denotes the total energy of gas phase oxygen molecule in the ground state.

S2. Supplementary Text

Table S1. ICP results of the samples.

Samples	A amount wt %	B amount wt %
$La_2Ti_2O_7$	74.01	24.68
$Nd_2Ti_2O_7$	74.85	24.12
$Sm_2Ti_2O_7$	75.41	23.74
$Gd_2Ti_2O_7$	75.84	22.93
$Er_2Ti_2O_7$	77.19	22.14
$Yb_2Ti_2O_7$	76.46	21.37
$La_2Sn_2O_7$	53.81	44.98
$Nd_2Sn_2O_7$	53.85	45.15
$Sm_2Sn_2O_7$	54.68	43.02
$Gd_2Sn_2O_7$	55.46	42.16
$Er_2Sn_2O_7$	57.18	40.09
$Yb_2Sn_2O_7$	58.09	39.81
$La_2Zr_2O_7$	60.04	39.54
$Nd_2Zr_2O_7$	61.26	37.54
$Sm_2Zr_2O_7$	61.04	36.46
$Gd_2Zr_2O_7$	62.07	36.21
$Er_2Zr_2O_7$	64.71	35.59
$Yb_2Zr_2O_7$	64.81	33.72
$La_2Ce_2O_7$	48.19	49.46
$Nd_2Ce_2O_7$	50.01	48.04
$Sm_2Ce_2O_7$	50.34	47.41
$Gd_2Ce_2O_7$	51.88	46.02
$Er_2Ce_2O_7$	53.22	45.08
$Yb_2Ce_2O_7$	54.39	43.74

Table S2. Electronegativity of elements at A-site and B-site.

A-site element	Electronegativity	B-site element	Electronegativity	O	Electronegativity
La	1.10	Ti	1.54	O	3.44
Nd	1.14	Sn	1.96		
Sm	1.17	Zr	1.33		
Gd	1.20	Ce	1.12		
Er	1.24				
Yb	1.30				