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Supplementary Information for:

Structural and Electronic Properties of $LnSi_n$ (n=5, 10; Ln=Sm, Eu, Yb) clusters: Density functional theory calculations

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Table S1. The composition (%) of inserted atom Ln and the Si_5/Si_{10} skeleton to the HOMO, LUMO orbitals, and the energy gap (eV) of $SmSi_5$, $EuSi_5$, $SmSi_{10}$ and $EuSi_{10}$ at unrestricted open-shell system.

Cluster	α-HOMO		α-LUMO		α-Gap	β-HOMO		β-LUMO		β-Gap
	Ln	$Si_{5/10}$	Ln	$Si_{5/10}$		Ln	$Si_{5/10}$	Ln	$Si_{5/10}$	
$SmSi_5$	9.6	90.4	77.1	22.9	2.24	5.0	95.0	77.8	22.2	2.45
$EuSi_5$	6.6	93.4	76.6	23.4	2.20	4.8	95.2	77.5	22.5	2.41
$SmSi_{10}$	3.9	96.1	73.1	26.9	2.25	3.6	96.4	74.3	25.7	2.42
$EuSi_{10}$	3.6	96.4	72.4	27.6	2.22	3.5	96.5	73.8	26.2	2.41

Table S2. The composition (%) of inserted atom Yb and the Si_5/Si_{10} skeleton to the HOMO, LUMO orbitals, and the energy gap (eV) of $YbSi_5$ and $YbSi_{10}$ at closed shell system.

Cluster	HOMO		LUMO		Gap
	Yb	$Si_{5/10}$	Yb	$Si_{5/10}$	
$YbSi_5$	4.7	95.3	72.6	27.4	2.72
$YbSi_{10}$	3.2	96.8	69.9	30.1	2.72

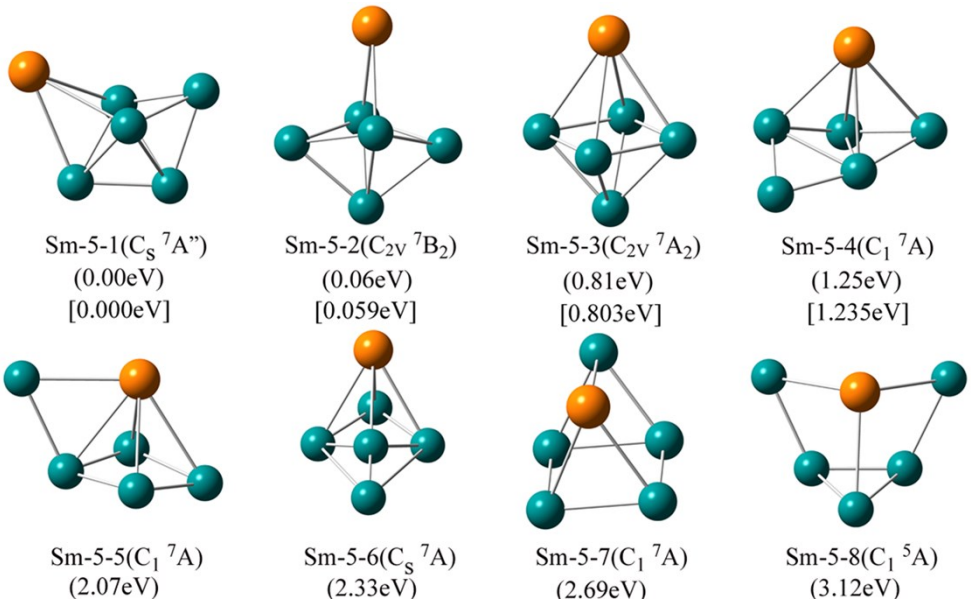


Figure S1. The various geometrical structures with the symmetry, electron state and relative energy of $SmSi_5$ at B3LYP/Ln/ECP28MWB//Si/6-311G(d) level. The relative energy excluding/including the ZPE correction are shown in parentheses/ square bracket, respectively.

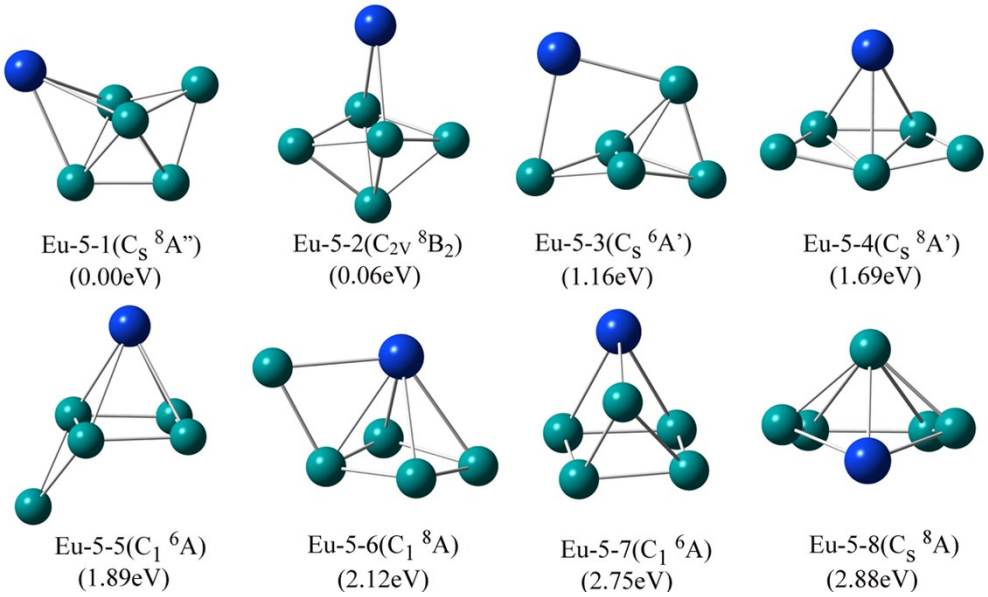


Figure S2. The various geometrical structures with the symmetry, electron state and relative energy of $EuSi_5$ at B3LYP/Ln/ECP28MWB//Si/6-311G(d) level.

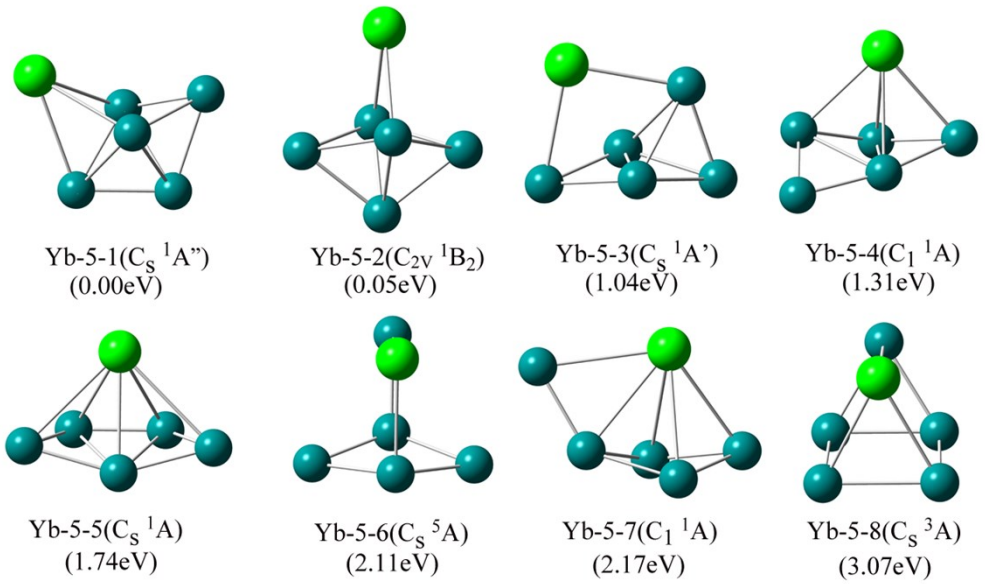
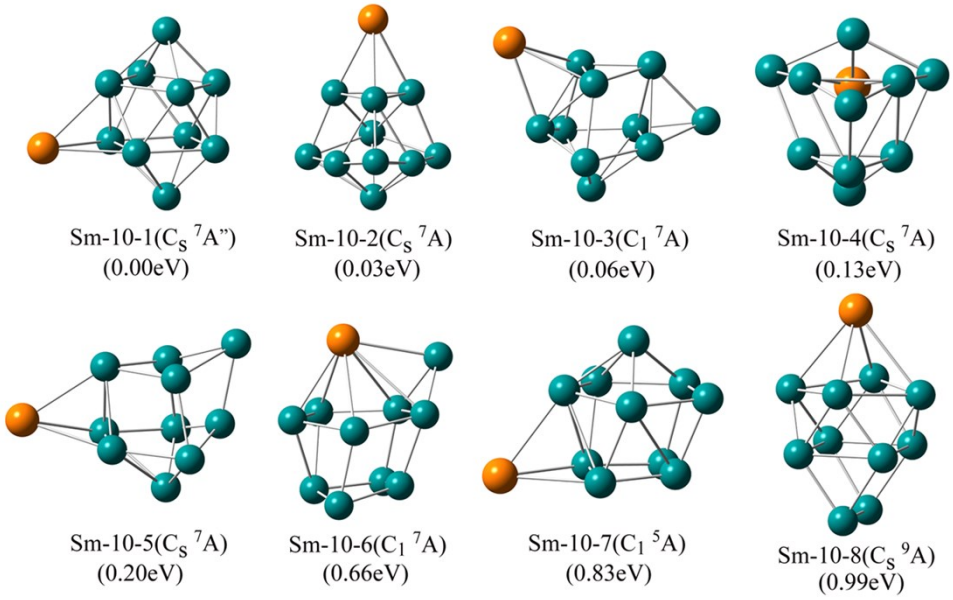


Figure S3. The various geometrical structures with the symmetry, electron state and relative energy of $YbSi_5$ at B3LYP/Ln/ECP28MWB//Si/6-311G(d) level.



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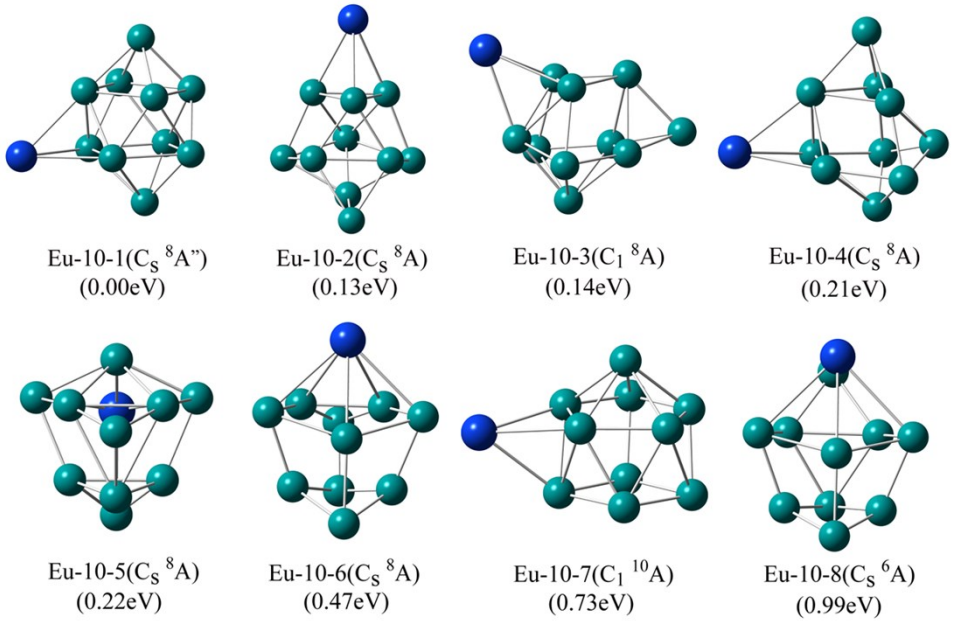

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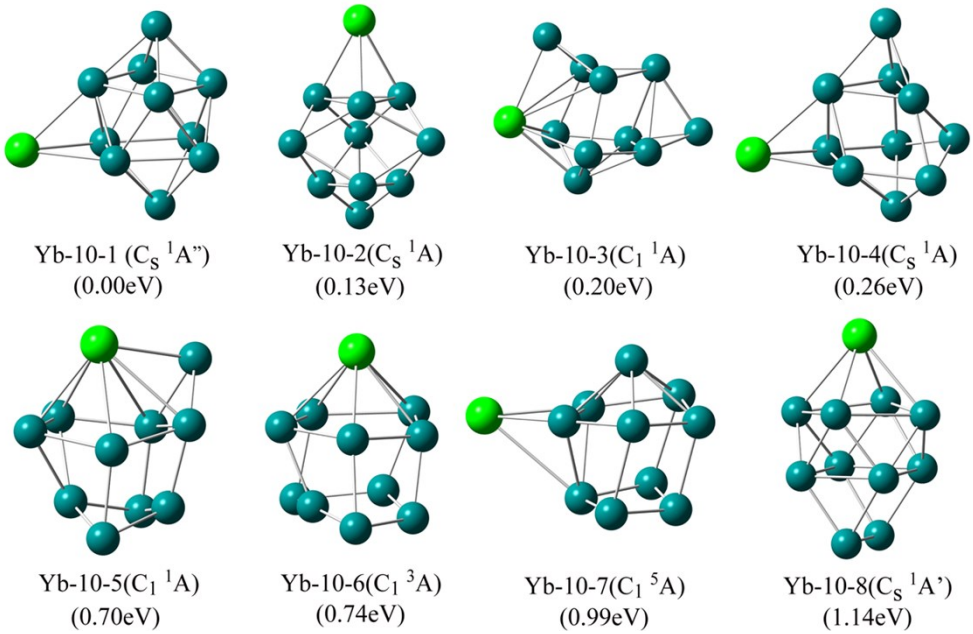

Figure S6. The various geometrical structures with the symmetry, electron state and relative energy of $YbSi_{10}$ at B3LYP/Ln/ECP28MWB//Si/6-311G(d) level.

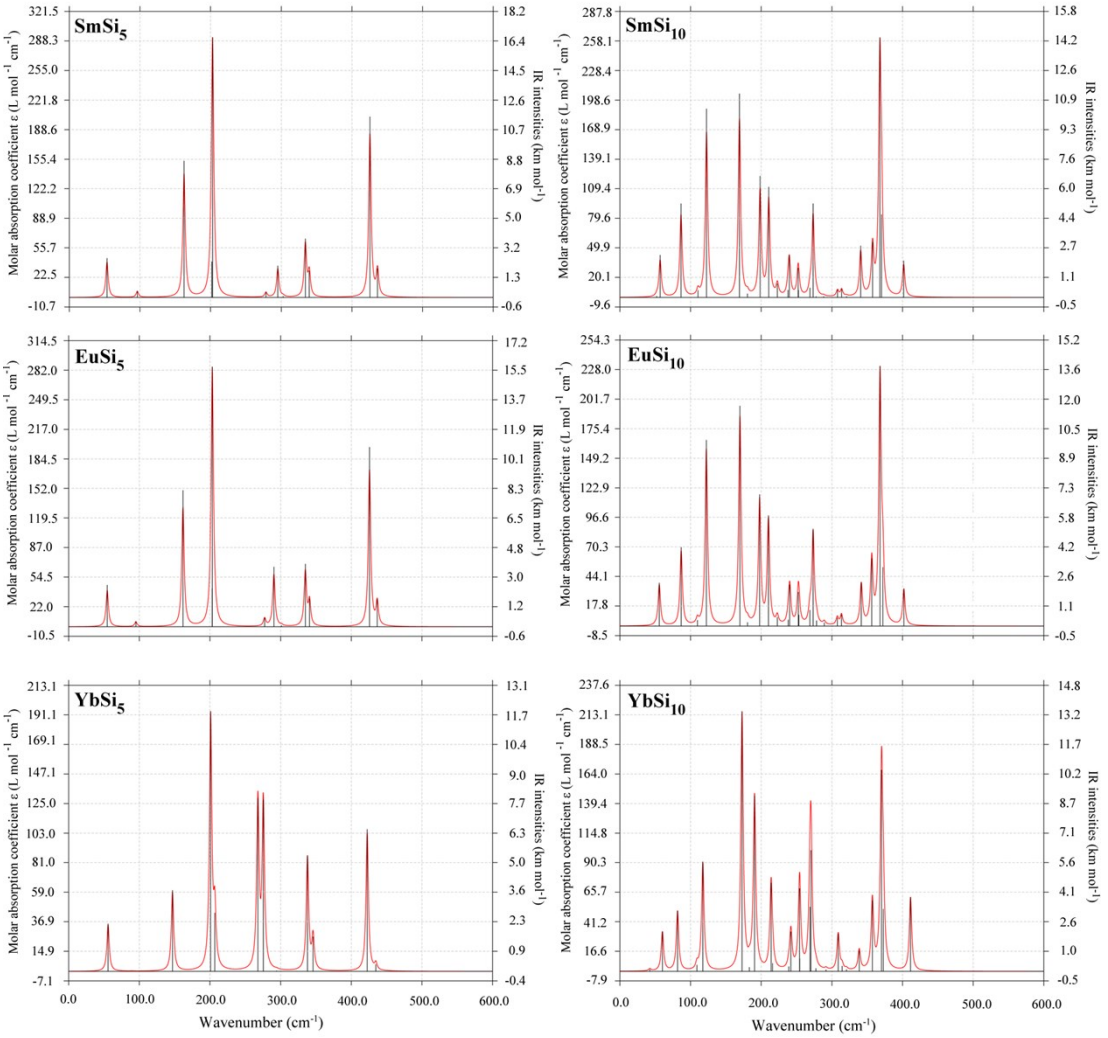

Figure S7. Infrared (IR) spectra of ground state structure of $LnSi_n$ (n=5, 10; Ln=Sm, Eu, Yb). The red curve corresponds to molar absorption coefficient, while the black spikes correspond to theoretically calculated IR intensities.

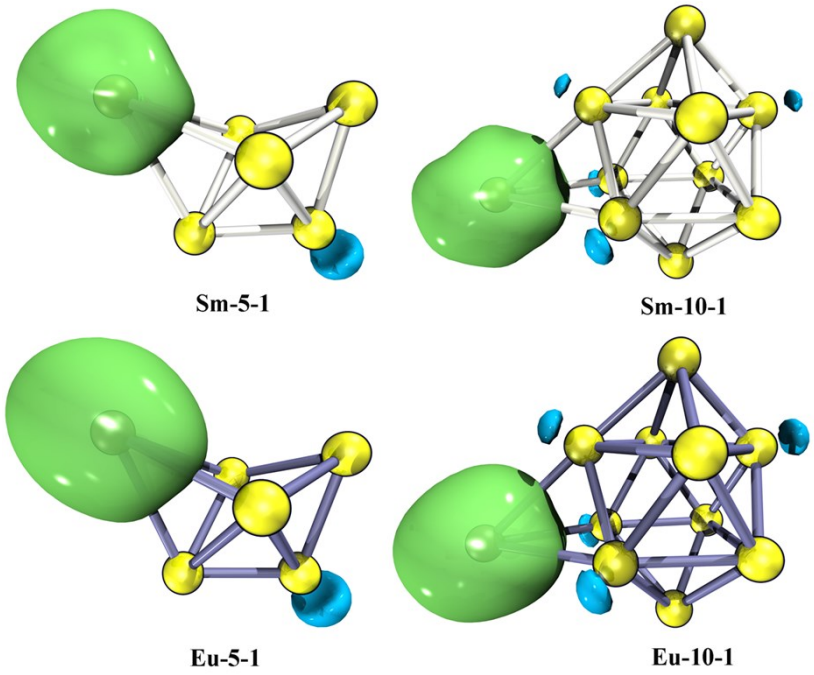

Figure S8. The spin density (ρ_{alpha} - ρ_{beta}) isosurfaces of ground state structure of $SmSi_n$ and $EuSi_n$. The isosurface is set to 0.02.

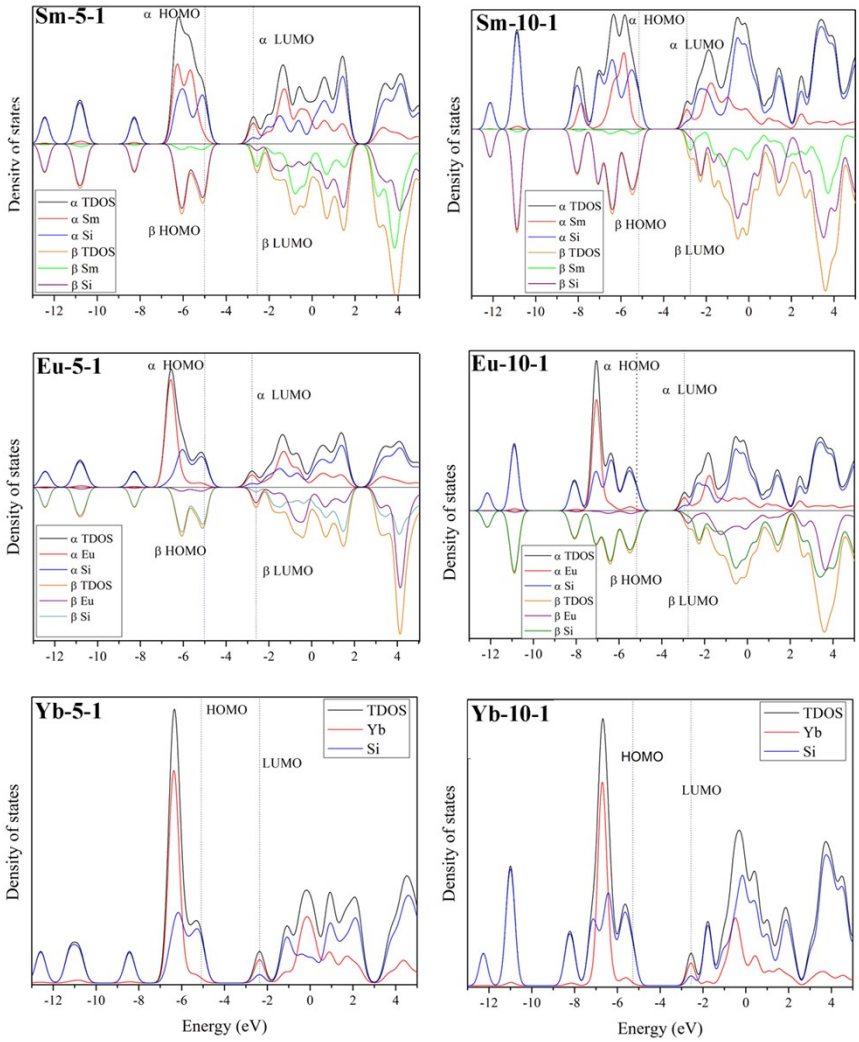

Figure S9. The total density of states (TDOS) and partial density of states (PDOS) maps for ground state $LnSi_n$. A Gaussian function with full width at half maximum (FWHM) of 0.5 eV was used for broadening molecular orbital energies to yield the DOS curves.

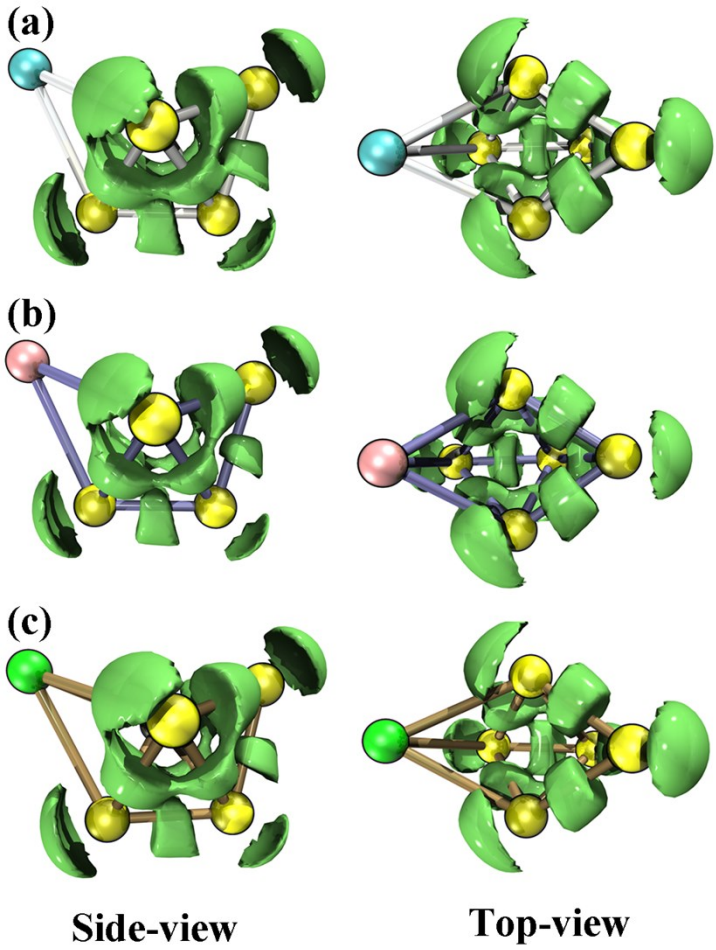

Figure S10. Isosurface maps of localized orbital locator (LOL) of ground state structure of $LnSi_5$. The isosurface is set to 0.548. The symbols (a), (b) and (c) indicate the $SmSi_5$, $EuSi_5$ and $YbSi_5$ systems, respectively.

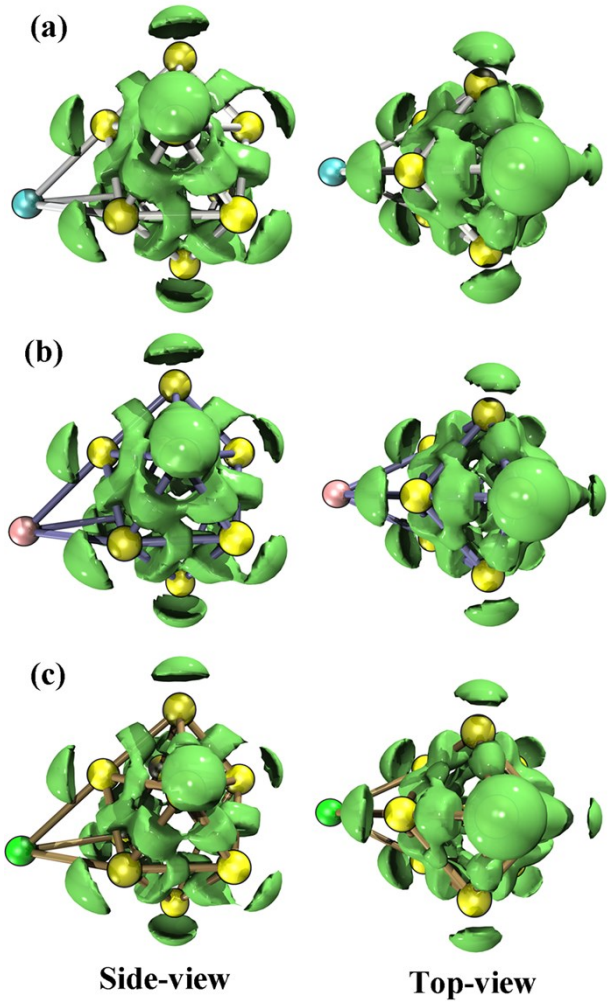

Figure S11. Isosurface maps of localized orbital locator (LOL) of ground state structure of $LnSi_{10}$. The isosurface is set to 0.548. The symbols (a), (b) and (c) indicate the $SmSi_{10}$, $EuSi_{10}$ and $YbSi_{10}$ systems, respectively.

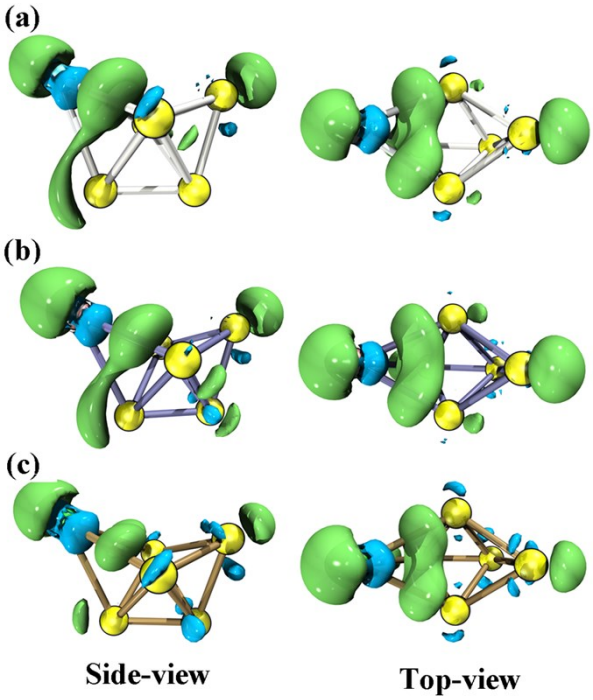

Figure S12. Isosurface maps of electron density difference (EDD) of ground state structure of $LnSi_5$. The isosurface is set to 0.0063 and -0.0048. Blue and green isosurfaces represent the electron density is reduced and increased, respectively. The symbols (a), (b) and (c) indicate the $SmSi_5$, $EuSi_5$ and $YbSi_5$ systems, respectively.

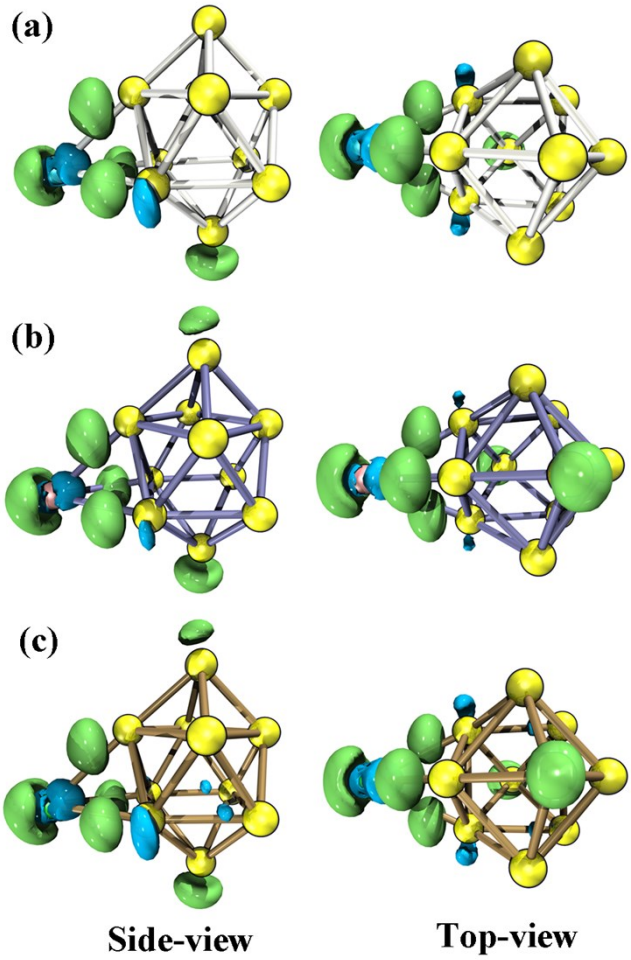

Figure S13. Isosurface maps of electron density difference (EDD) of ground state structure of $LnSi_{10}$. The isosurface is set to 0.0063 and -0.0048. Blue and green isosurfaces represent the electron density is reduced and increased, respectively. The symbols (a), (b) and (c) indicate the $SmSi_{10}$, $EuSi_{10}$ and $YbSi_{10}$ systems, respectively.

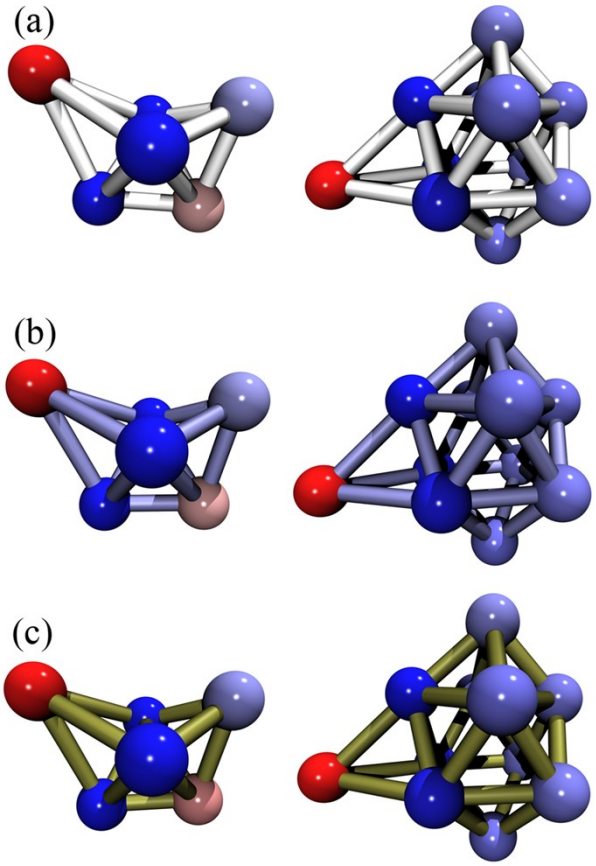

Figure S14. Atom coloring diagram of ground state structure of $LnSi_n$. The atomic color is red and blue to indicate the atomic charge is positive and negative, respectively. The darker the color, the greater the value. The symbols (a), (b) and (c) indicate the $SmSi_n$, $EuSi_n$ and $YbSi_n$ systems, respectively.