Supporting Information for: Ab-initio Study of Oxygen Vacancy Stability in Bulk and Cerium-doped Lutetium Oxyorthosilicate

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Abstract

We study from first principles the stability of neutral and charged oxygen vacancies in lutetium oxyorthosilicate, Lu_2SiO_5, as well as its possible modification due to the presence of Ce^{3+}, as present in commercial scintillators. We show that the neutral oxygen vacancies with the lowest formation energy form at the oxygen sites within the $[SiO_4]$ tetrahedra instead of the interstitial oxygen site bonded exclusively to lutetium atoms. The discrepancy with a previous study is attributed to the quality of the pseudopotential. Support for these results is found by performing a bonding analysis of the oxygen sites, as well as oxygen vacancy calculations in the iso-structural Y_2SiO_5 compound. In addition, we find that the incorporation of Ce^{3+} ion does not affect the stability of oxygen vacancies in Lu_2SiO_5.

Keywords: Scintillator, Oxygen vacancy, luminescence, ab-initio calculation

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Table 1: Lattice parameters of bulk LSO within the conventional cell.

LSO	a(Å)	b(Å)	c(Å)	α	β	γ	Volume(Å^3)
Exp.	14.28	6.64	10.25	90.00	122.22	90.00	821.74
Cal.(LDA-TM)	14.95	6.84	10.81	90.00	122.99	90.00	927.53
Cal.(LDA-FHI)	14.06	6.38	9.85	90.00	122.76	90.00	743.52
Cal.(LDA-Dojo)	14.12	6.15	10.03	90.00	122.25	90.00	781.28

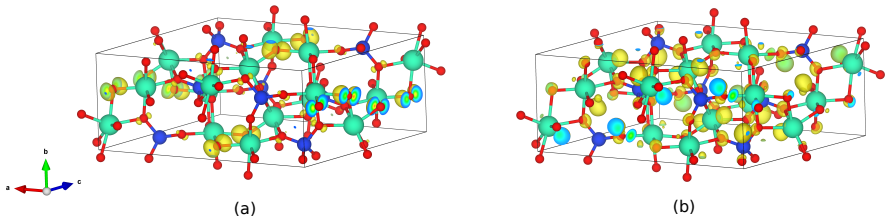

Figure 1: Charge density of (a) VBM and (b) CBM of Lu_2SiO_5 at the Γ point. The green, blue and red spheres stand for the Lu, Si and O atoms, respectively.

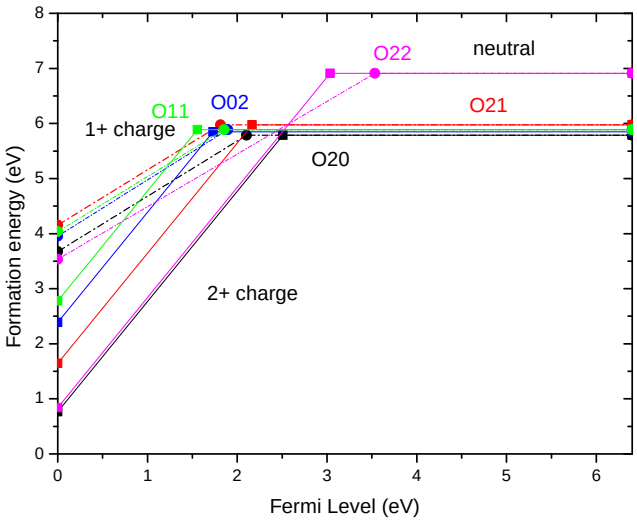

Figure 2: The corrected formation energy of oxygen vacancy with 2+, 1+ and neutral charge in Lu_2SiO_5 from PBE-GGA PAW, using 63-atom supercell.

Table 2: Relaxed O-Lu and O-Si bond length of five oxygen crystallographic sites in LSO crystal. The longest O-Lu is shown in bold. [Unit: Å]

	M = O_{20}	M = O_{21}	M = O_{11}	M = O_{02}	M = O_{22}
M-Lu_1	2.307	**2.732**	2.254	—	2.352
	2.235	2.325			2.144
M-Lu_2	—	2.216	2.237	2.236	2.271
				2.224	2.57
M-Si	1.615	1.612	1.624	1.641	—

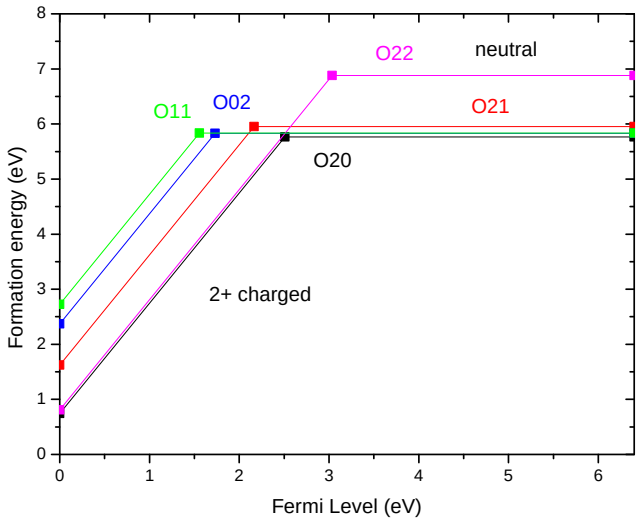

Figure 3: Formation energy of oxygen vacancy in Lu_2SiO_5 from PBE-PAW, using 127-atom supercell.

Table 3: The formation energy of neutral oxygen vacancies in LSO bulk. [Unit: eV]

case	E_{tot}(LSO:V_O, 63-atoms.)	$\Delta E_{f,1}$ (63-atom)	E_{tot}(LSO:V_O, 127-atom)	$\Delta E_{f,1}$ (127-atom)
V_{O20}	-36516.14	5.76	-73475.39	5.76
V_{O21}	-36515.95	5.97	-73475.21	5.95
V_{O11}	-36516.04	5.86	-73475.30	5.83
V_{O02}	-36516.08	5.82	-73475.33	5.83
V_{O02}	-36515.01	6.88	-73474.28	6.88

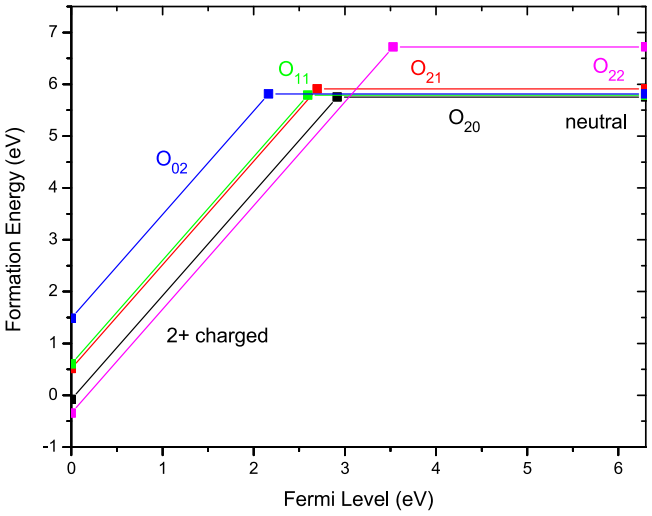

Figure 4: Formation energy of oxygen vacancy in Y_2SiO_5 from PBE-PAW, using 63-atom supercell.