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Meta-generalized gradient approximation time-dependent density-functional theory study of electron trapping in Hf- and Zr-doped lutetium oxide: influencing the oxygen vacancy

Andrii Shyichuk

Meta-GGA TD-DFT study on electron trapping in Hf and Zr doped lutetium oxide: influencing the oxygen vacancy

A. Shyichuk

Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland

* andrii.shyichuk@chem.uni.wroc.pl, +48 71 375 7265
* corresponding author:

Supplementary information

Geometry optimization

Quantum Espresso 6.5, 6.6 and 7.1 (QE, *https://www.quantum-espresso.org/*) module pw.x (total energy calculations and geometry optimization) was used with mostly default settings. Perdew-Zunger local density approximation (LDA) functional (*10.1103/PhysRevB.23.5048*) was used. Crucial settings are shown in Table S1. The results should be reproducible with either of codes.

Table S1. Selected settings used in Quantum Espresso calculations.

Section &CONTROL	
calculation	'vc-relax'
etot_conv_thr	1E-5
forc_conv_thr	0.0001
nstep	700

Section &SYSTEM	
ecutwfc	40
ecutrho	400
occupations	'smearing'
smearing	'gaussian'
degauss	0.001
nspin	1 or 2 *
tot_charge	2 / 1 / 0 / –1 / –2 *

Section &ELECTRONS	
electron_maxstep	200
conv_thr	1.0D-7
diago_thr_init	1.0E-4
startingpot	'atomic'
mixing_mode	'plain'
mixing_beta	0.5
mixing_ndim	8
diagonalization	'david'

Section &IONS	
ion_dynamics	'bfgs'

Section &CELL	
cell_dynamics	'bfgs'

* tot_charge is total charge on the system, while nspin controls spin polarization (1 for unpolarized and 2 for polarized); spin-polarization was used for systems with odd tot_charge.

Pseudopotentials

The pseudopotentials (PPs) used were ultrasoft (USPP), generated by the Vanderbilt code version 7.3.6. The oxygen PP recipe (PP generation input file) from GBRV group (*10.1016/j.commatsci.2013.08.053*), version 1.2 was used. The Lu USPP recipe was kindly provided by co-author of the GBRV set, Kevin F. Garrity. The potential had the 4f electrons in core; the valence electrons were effectively of a *d*-element, not an *f*-element. Hf^{4+} USPP was used. Zr default (general purpose) GBRV USPP was used. For test purposes, custom Zr^{4+} USPP (analogous to the Hf^{4+} USPP) was prepared, but the respective results are only shown Table S5 below.

Initial geometry of Lu_2O_3 cell

Initial geometry (in the from of fractional coordinates of atoms) was generated by Spacegroup code shipped with Elk code version 4.3.6 (*http://elk.sourceforge.net/*), using space group Ia-3, all cell angles of 90.0 degrees and the following fractional coordinates of atoms (*10.3390/ma7107059*):

Lu1: 0.25, 0.25, 0.25

Lu2: 0.46685, 0.0, 0.25

O: 0.39159, 0.15282, 0.38011

Positions of the rest of the atoms were generated by the symmetry operations respective to the space group. Note that Lu1 and Lu2 here are site labels, not to be confused with the atom labels used below. The geometry from Spacegroup code was optimized using QE and shown in Table S2. Cell dimension was 19.432845 bohr.

Table S2. The initial geometry used in the calculations (fractional coordinates).

Atom label	fc1	fc2	fc3	Atom label	fc1	fc2	fc3
Lu1	0.2499998	0.2499998	0.2499998	O41	0.3912785	0.8476405	0.1200032
Lu2	0.7500002	0.7500002	0.7500002	O42	0.8912793	0.3476402	0.6200032
Lu3	0.7500004	0.2500000	0.2499994	O43	0.6087215	0.1523595	0.8799968
Lu4	0.2499996	0.7500000	0.7500006	O44	0.1087207	0.6523598	0.3799968
Lu5	0.2499994	0.7500004	0.2500000	O45	0.6087213	0.6523598	0.1200033
Lu6	0.7500006	0.2499996	0.7500000	O46	0.1087210	0.1523596	0.6200034
Lu7	0.7500000	0.7500006	0.2499996	O47	0.3912787	0.3476402	0.8799967
Lu8	0.2500000	0.2499994	0.7500004	O48	0.8912790	0.8476404	0.3799966
Lu9	0.4664097	0.0000001	0.2499996	O49	0.3799966	0.3912785	0.1523596
Lu10	0.9664106	0.4999998	0.7500001	O50	0.8799967	0.8912790	0.6523597
Lu11	0.5335903	-0.0000001	0.7500004	O51	0.6200034	0.6087215	0.8476404
Lu12	0.0335894	0.5000002	0.2499999	O52	0.1200033	0.1087210	0.3476403
Lu13	0.5335896	0.5000000	0.2500000	O53	0.3799966	0.6087216	0.3476403
Lu14	0.0335890	0.0000003	0.7500004	O54	0.8799966	0.1087207	0.8476408
Lu15	0.4664104	0.5000000	0.7500000	O55	0.6200034	0.3912784	0.6523597
Lu16	0.9664110	-0.0000003	0.2499996	O56	0.1200034	0.8912793	0.1523592
Lu17	0.2499996	0.4664097	0.0000001	O57	0.1200032	0.3912785	0.8476405
Lu18	0.7500001	0.9664106	0.4999998	O58	0.6200032	0.8912793	0.3476402
Lu19	0.7500004	0.5335903	-0.0000001	O59	0.8799968	0.6087215	0.1523595
Lu20	0.2499999	0.0335894	0.5000002	O60	0.3799968	0.1087207	0.6523598
Lu21	0.2500000	0.5335896	0.5000000	O61	0.1200033	0.6087213	0.6523598
Lu22	0.7500004	0.0335890	0.0000003	O62	0.6200034	0.1087210	0.1523596
Lu23	0.7500000	0.4664104	0.5000000	O63	0.8799967	0.3912787	0.3476402
Lu24	0.2499996	0.9664110	-0.0000003	O64	0.3799966	0.8912790	0.8476404
Lu25	0.0000001	0.2499996	0.4664097	O65	0.1523596	0.3799966	0.3912785
Lu26	0.4999998	0.7500001	0.9664106	O66	0.6523597	0.8799967	0.8912790
Lu27	-0.0000001	0.7500004	0.5335903	O67	0.8476404	0.6200034	0.6087215
Lu28	0.5000002	0.2499999	0.0335894	O68	0.3476403	0.1200033	0.1087210
Lu29	0.5000000	0.2500000	0.5335896	O69	0.3476403	0.3799966	0.6087216
Lu30	0.0000003	0.7500004	0.0335890	O70	0.8476408	0.8799966	0.1087207
Lu31	0.5000000	0.7500000	0.4664104	O71	0.6523597	0.6200034	0.3912784
Lu32	-0.0000003	0.2499996	0.9664110	O72	0.1523592	0.1200034	0.8912793
O33	0.3912785	0.1523596	0.3799966	O73	0.8476405	0.1200032	0.3912785
O34	0.8912790	0.6523597	0.8799967	O74	0.3476402	0.6200032	0.8912793
O35	0.6087215	0.8476404	0.6200034	O75	0.1523595	0.8799968	0.6087215
O36	0.1087210	0.3476403	0.1200033	O76	0.6523598	0.3799968	0.1087207
O37	0.6087216	0.3476403	0.3799966	O77	0.6523598	0.1200033	0.6087213
O38	0.1087207	0.8476408	0.8799966	O78	0.1523596	0.6200034	0.1087210
O39	0.3912784	0.6523597	0.6200034	O79	0.3476402	0.8799967	0.3912787
O40	0.8912793	0.1523592	0.1200034	O80	0.8476404	0.3799966	0.8912790

Anionic and cationic voids

The crystal properties of the voids are similar to those of the anions and cations. There are namely 8 cationic voids of C_{3i} symmetry and 24 cationic voids of C_2 symmetry, generated by the cell symmetry operations from position fc. 0, 0, 0 and 0, 0.25, 0.25, respectively. The anionic voids were generated from a position fc. 0.375, 0.375, 0.375. The list is given below, in Table S3.

Table S3. Anionic void (interstitial oxygen) and cationic void sites in c-Lu2O3

Site label	fc1	fc2	fc3	Site symmetry
Oi1	0.375	0.375	0.375	C_1
Oi2	0.875	0.875	0.875	C_1
Oi3	0.625	0.625	0.625	C_1
Oi4	0.125	0.125	0.125	C_1
Oi5	0.625	0.125	0.375	C_1
Oi6	0.125	0.625	0.875	C_1
Oi7	0.375	0.875	0.625	C_1
Oi8	0.875	0.375	0.125	C_1
Oi9	0.375	0.625	0.125	C_1
Oi10	0.875	0.125	0.625	C_1
Oi11	0.625	0.375	0.875	C_1
Oi12	0.125	0.875	0.375	C_1
Oi13	0.625	0.875	0.125	C_1
Oi14	0.125	0.375	0.625	C_1
Oi15	0.375	0.125	0.875	C_1
Oi16	0.875	0.625	0.375	C_1
CV1	0	0	0	C_{3i}
CV2	0.5	0.5	0.5	C_{3i}
CV3	0	0.5	0	C_{3i}
CV4	0.5	0	0.5	C_{3i}
CV5	0	0	0.5	C_{3i}
CV6	0.5	0.5	0	C_{3i}
CV7	0	0.5	0.5	C_{3i}
CV8	0.5	0	0	C_{3i}
CV9	0	0.25	0.25	C_2
CV10	0.5	0.75	0.75	C_2
CV11	0	0.75	0.75	C_2
CV12	0.5	0.25	0.25	C_2
CV13	0	0.75	0.25	C_2
CV14	0.5	0.25	0.75	C_2
CV15	0	0.25	0.75	C_2
CV16	0.5	0.75	0.25	C_2
CV17	0.25	0	0.25	C_2
CV18	0.75	0.5	0.75	C_2
CV19	0.75	0	0.75	C_2
CV20	0.25	0.5	0.25	C_2
CV21	0.25	0	0.75	C_2
CV22	0.75	0.5	0.25	C_2
CV23	0.75	0	0.25	C_2
CV24	0.25	0.5	0.75	C_2
CV25	0.25	0.25	0	C_2
CV26	0.75	0.75	0.5	C_2
CV27	0.75	0.75	0	C_2
CV28	0.25	0.25	0.5	C_2
CV29	0.75	0.25	0	C_2
CV30	0.25	0.75	0.5	C_2
CV31	0.25	0.75	0	C_2
CV32	0.75	0.25	0.5	C_2

FP-LAPW calculations

Calculations with Elk 7.0.12 or 8.5.02 used species files provided with the code. Only oxygen species file was modified – the local orbital with lorbl = 0 and lorbord = 3 was removed, resulting in total of two local orbitals with fixed linearization energies for oxygen. The muffin-tin radius for Lu was 2.0 bohr (2.3 bohr in some of the latter cases), and 1.45 bohr for O. Other non-default options are specified in Table S4. Note that, due to the use of atomic units, electron charge in elk is +1, while proton charge is –1. Consequently, e.g. "*chgexs* -2" means two additional holes in the system, while "*chgexs* 1" means one additional electron. The value of *rgkmax* (defines maximum |**G**+**k**| for APW functions) was 7.9-8.3, depending on the system. The value of *gmaxvr* (maximum |**G**| for potential and density) was 17. Smoothing operations to the exchange-correlation potentials were applied using *msmooth* value 4. Fixed spin magnetization (FSM) was used via *fsmtype* 1 and *msmooth* 0. 0. *X*, where *X* was the total cell magnetization(i.e. the number of unpaired electrons), directed up along *z* axis. In the calculation without FSM, Broyden mixing (default) was used, but the mixing parameters set via *broydpm* were reduced. The k-point grid was 3×3×3. Convergence threshold was twofold: root mean square change from last three iterations in Kohn-Sham potential was required to be lower than $1 \cdot 10^{-6}$ a.u., change in total energy was required to be lower than $1 \cdot 10^{-4}$ a.u..

Table S4. Selected settings used in Elk code.

Variable name	Value	Variable name	Value
tasks	0, 10	chgexs	-2 / -1 / 0 / 1 / 2
xctype	100 209 9	fsmtype	1
gmaxvr	17	momfix	0. 0. 1. or 0. 0. 2.
rgkmax	7.9 - 8.3	ngridk	3 3 3
msmooth	4	spinpol	f / t
isgkmax	-2	lradstp	2
broydpm	0.2 0.075 (or 0.1 0.0375)	dosmsum	t

The *xctype* option selects Räsänen, Pittalis and Proetto mGGA for exchange (209) and PZ correlation (9) from libxc (100).

Dopant, vacancy and interstitial sites

The sites for the impurities were selected so that different structures had something in common. Hf/Zr initial C_{3i} site was [0.75, 0.75, 0.75]. Hf/Zr initial C_2 site was [0.4664104, 0.5, 0.75].

Table S5. Defect positions, file names, defect-defect distances (Angstrom, optimized cells) and cell charges

File name	O/V_O initial position		O_i initial position	R(Hf-V_O)	R(Hf-O_i)	R(V_O-O_i)	Charge
LHf1vc1	[0.6200034, 0.6087215, 0.8476404]	2.215		2.19			1
LHf1cc1	[0.6523597, 0.6200034, 0.3912784]	4.050		4.31			1
LHf1ac1	[0.1200033, 0.6087213, 0.6523598]	4.195		4.13			1
LHf1bc1	[0.6087215, 0.1523595, 0.8799968]	4.585		4.32			1
LHf1uc1	[0.1200033, 0.108721, 0.3476403]	6.723		6.70			1
LHf1wc1	[0.3799966, 0.891279, 0.8476404]	4.195		4.13			1
LHf1wc1H				4.12			1
LHf1wAc0			[0.625, 0.625, 0.625]	4.13	2.07	4.40	0
LHf1wAc-1				4.14	2.08	4.42	-1
LHf1wAc-1H				4.13	2.08	4.42	-1
LHf1wAc-2				4.14	2.09	4.44	-2
LHf1wBc0			[0.875, 0.375, 0.125]	4.15	5.44	7.49	0
LHf1wBc-1				4.16	5.46	7.54	-1
LHf1wBc-1H				4.16	5.45	7.53	-1
LHf1wBc-2				4.21	5.47	7.57	-2
LZr1vc1h4	[0.6200034, 0.6087215, 0.8476404]	2.215		2.23			1
LZr1vc1h				2.23			1
LZr1wc1h4	[0.3799966, 0.891279, 0.8476404]	4.195		4.12			1
LZr1wc1h				4.12			1
LZr1wAc0h			[0.625, 0.625, 0.625]	4.12	2.02	4.39	0
LZr1wBc0h			[0.875, 0.375, 0.125]	4.14	5.43	7.48	0
LHf2vc1	[0.6200034, 0.6087215, 0.8476404]	2.180		2.38	0.00	0.00	1
LHf2ac1	[0.1200033, 0.6087213, 0.6523598]	3.866		3.99	0.00	0.00	1
LHf2bc1	[0.6087215, 0.1523595, 0.8799968]	4.088		4.36	0.00	0.00	1
LHf2cc1	[0.6523597, 0.6200034, 0.3912784]	4.334		4.45	0.00	0.00	1
LHf2uc1	[0.1200033, 0.108721, 0.3476403]	6.782		6.49	0.00	0.00	1
LHf2wc1	[0.3799966, 0.891279, 0.8476404]	4.241		4.04	0.00	0.00	1
LHf2wAc0			[0.625, 0.625, 0.625]	4.01	2.09	4.41	0
LHf2wAc-1				4.03	2.10	4.43	-1
LHf2wAc-1H				4.04	2.10	4.44	-1
LHf2wAc-2				4.06	2.11	4.45	-2
LHf2wBc0			[0.875, 0.375, 0.125]	4.05	5.88	7.49	0
LHf2wBc-1				4.07	5.90	7.54	-1
LHf2wBc-1H				4.08	5.89	7.54	-1
LHf2wBc-2				4.10	5.92	7.59	-2
LZr2vc1h4	[0.6200034, 0.6087215, 0.8476404]	2.180		2.42	0.00	0.00	1
LZr2vc1h				2.41	0.00	0.00	1
LZr2wc1h4	[0.3799966, 0.891279, 0.8476404]	4.241		4.04	0.00	0.00	1
LZr2wc1h				4.04	0.00	0.00	1
LZr2wAc0h			[0.625, 0.625, 0.625]	4.01	2.03	4.40	0
LZr2wBc0h			[0.875, 0.375, 0.125]	4.05	5.88	7.48	0