Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary information

The local atomic structure and thermoelectric properties of Ir-doped ZnO: hybrid DFT calculations and XAS experiments

Andrei Chesnokov[a], Denis Gryaznov*[a], Natalia V. Skorodumova[b,c] , Eugene A. Kotomin[a,d] , Andrea Zitolo[e], Martins Zubkins[a] , Alexei Kuzmin[a], Andris Anspoks[a] and Juris Purans[a]

[a] Institute of Solid State Physics, University of Latvia, Kengaraga 8, Riga, LV-1063, Latvia
[b] Department of Materials Science and Engineering, School of Industrial Engineering and Management, KTH-Royal Institute of Technology, Brinellvägen 23, Stockholm, Sweden
[c] Department of Physics and Astronomy, Uppsala University, Box 516, 751 20 Uppsala, Sweden
[d] Max Planck Institute for Solid State Research, Heisenbergstr. 1, Stuttgart, D-70569, Germany
[e] Synchrotron SOLEIL, L'orme des Merisiers, BP 48 Saint Aubin, 91192, Gif-sur-Yvette, France

Basis sets were obtained from the following sources:

- Ir: Basis Set Exchange Resource[1], specifically, LANL2TZ(f) as used in Ping *et al.*[2]
- O: Ping *et al.*[2]
- Zn: Gryaznov *et al.*[3]

Emphasized coefficients in the Zn basis set were optimized with OPTBAS program[4] (see main text for details).

Ir	Zn	O
277 12	30 8	8 5
INPUT	0 0 8 2.0 1.0	0 0 7 2. 1.
17 5 6 5 5 5 0	417016.5 0.00023	7817.0000000 0.0011760
823.5880147 -0.1578014 -1	60504.2 0.00192	1176.0000000 0.0089680
364.6613336 -1517.5270446 0	12907.9 0.01101	273.2000000 0.0428680
55.7082801 -316.5306529 0	3375.74 0.04978	81.1700000 0.1439300
12.0464544 -91.8880941 0	1018.11 0.16918	27.1800000 0.3556300
3.5120610 -9.2241773 0	352.55 0.36771	9.5320000 0.4612480
188.0490770 3.1578014 -2	138.19 0.40244	3.4140000 0.1402060
340.4194712 26.8322577 -1	57.851 0.14386	0 0 2 2. 1.
128.2373673 800.4250007 0	0 1 6 8.0 1.0	9.5320000 -0.1541530
33.8644961 369.4050683 0	1079.2 -0.00620 0.00889	0.9398000 1.0569140
4.7560005 242.4171899 0	256.52 -0.07029 0.06384	0 0 1 0. 1.
3.9649974 -118.2173282 0	85.999 -0.13721 0.22039	0.2846000 1.0000000
289.7291139 2.1578014 -2	34.318 0.26987 0.40560	0 2 4 4. 1.
87.4633789 61.9678610 -1	14.348 0.59918 0.41370	35.1800000 0.0195800
30.4363766 269.0581986 0	4.7769 0.32239 0.34974	7.9040000 0.1242000
4.0553412 231.1654793 0	0 1 4 8.0 1.0	2.3050000 0.3947140
3.5525341 -133.6952667 0	60.891 0.00679 -0.00895	0.7171000 0.6273760
136.4017106 3.1578014 -2	25.082 -0.08468 -0.03333	0 2 1 0. 1.
95.0776925 45.9349803 -1	10.620 -0.34709 0.08119	0.2137000 1.0000000
49.2258410 359.0344668 0	4.3076 0.40633 0.56518	
15.0874145 176.4740119 0	0 1 1 2.0 1.0	
4.0405764 54.5155286 0	1.6868 1.0 1.0	

127.3507908 3.9546197 -2 66.2364374 52.9773655 -1 34.4299229 274.8643383 0 10.1995721 137.2047338 0 2.5409702 14.8633305 0 0 0 1 2. 1. 2.3500000 1.0000000 0 0 1 2. 1. 1.5820000 1.0000000 0 0 1 0. 1. 0.5018000 1.0000000 0 0 1 0. 1. 0.2500000 1.0000000 0 2 1 6. 1. 2.7920000 1.0000000 0 2 1 0. 1. 1.5410000 1.0000000 0 2 1 0. 1. 0.5100000 1.0000000 0 2 1 0. 1. 0.0980000 1.0000000 0 3 1 7. 1. 1.2400000 1.0000000 0 3 1 0. 1. 0.4647000 1.0000000 0 3 1 0. 1. 0.1529000 1.0000000 0 4 1 0. 1. 0.9380000 1.0000000	0 1 1 0.0 1.0 0.62668 1.0 1.0 0 1 1 0.0 1.0 *0.12729378183255* 1.0 1.0 0 3 4 10.0 1.0 57.345 0.02857 16.082 0.15686 5.3493 0.38663 1.7548 0.47766 0 3 1 0.0 1.0 *0.49499382987434* 1.0	

Geometry relaxation

After a full structure relaxation, the primitive unit cell of wurtzite ZnO has lattice constants *a*=3.2573 Å and *c*=5.1981 Å (experimental values are 3.2494 and 5.2054 Å, respectively[5]) and has a 3.45 eV wide bandgap (experimental value is 3.44 eV[6]).

Wyckoff positions of atomic coordinates in Ir-containing reference structures have free parameters. After a full structure relaxation, they are as follows:

IrO_2: rutile structure (space group $P4_2/mnm$) structure, [Ir: 2a; O: 4f (0.307, 0.307, 0)]

Ir_2O_3: corundum structure (space group $R\bar{3}c$), [Ir: 4c (0, 0, 0.350); O: 6e (0.702, 0, 0.25)] * Hexagonal axes

$ZnIr_2O_4$: spinel structure (space group $Fd\bar{3}m$), [Zn: 8a; Ir: 16d; O: 32e (0.2609, 0.2609, 0.2609)] * Standard setting (origin choice 2)

Table S1. Calculated and experimental bulk properties of IrO_2, Ir_2O_3, and $ZnIr_2O_4$. *a*, *c* are the lattice parameters, d_{Ir-O} is the Ir-O interatomic distance, q_{Ir} and q_O are effective atomic charges of Ir and O, respectively, μ_{Ir} and μ_{Ir} are their magnetic moments, ΔE is the bandgap value.

	***a*; *c*, Å**	d_{Ir-O}, **Å**	q_{Ir}, **e**	μ_{Ir}, **μ_B**	q_O, **e**	μ_O, **μ_B**	**ΔE, eV**	***a*; *c* exp, Å**	d_{Ir-O} **exp, Å**
IrO_2	4.471; 3.169	short: 1.942 long: 1.999	1.712	0.625	-0.856	0.171	None	4.505; 3.159[7]	short: 1.94-1.960 long: 1.999-2.00 [7,8]
Ir_2O_3	5.213; 13.848	short: 2.053 long: 2.085	1.241	0.000	-0.827	0.000	3.39	5.214-5.438 13.846 - 14.737[9]	1.53-1.57
$ZnIr_2O_4$	8.633	2.069	1.067	0.000	-0.824	0.000	3.44 (present) 2.97[10,a] 3.30[11,a]	8.503-8.507[10]	

Notes: a) experimental optical band gap

Spin densities

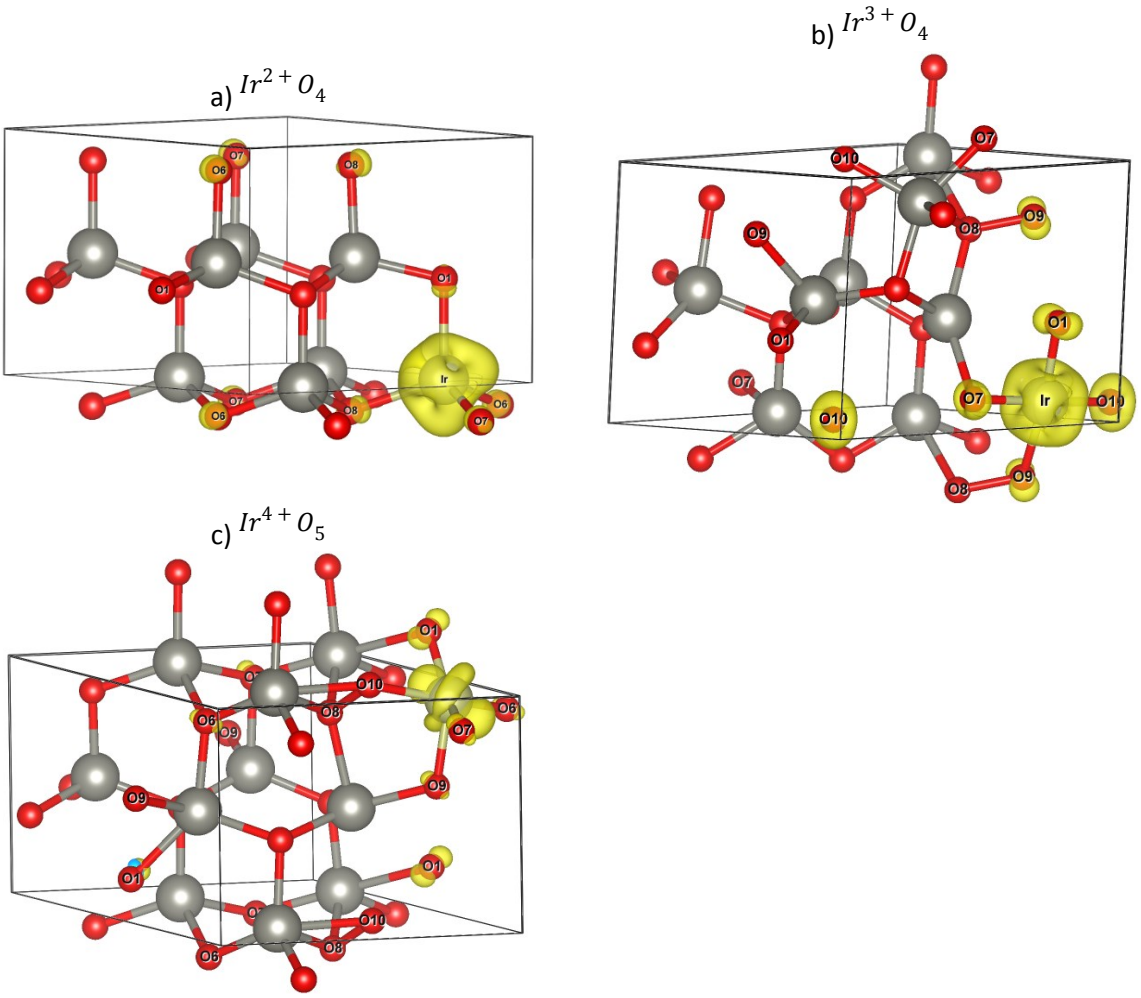

Fig. S1. Atomic structure and spin density distribution. Light yellow spheres represent Ir atoms, gray – Zn, and red – O atoms. Yellow clouds represent orbitals with unpaired electrons. The box marks the supercell boundaries. All named oxygen atoms are bound to Ir. All Ir-bound oxygen atoms have a nonzero spin.

Thermoelectric properties

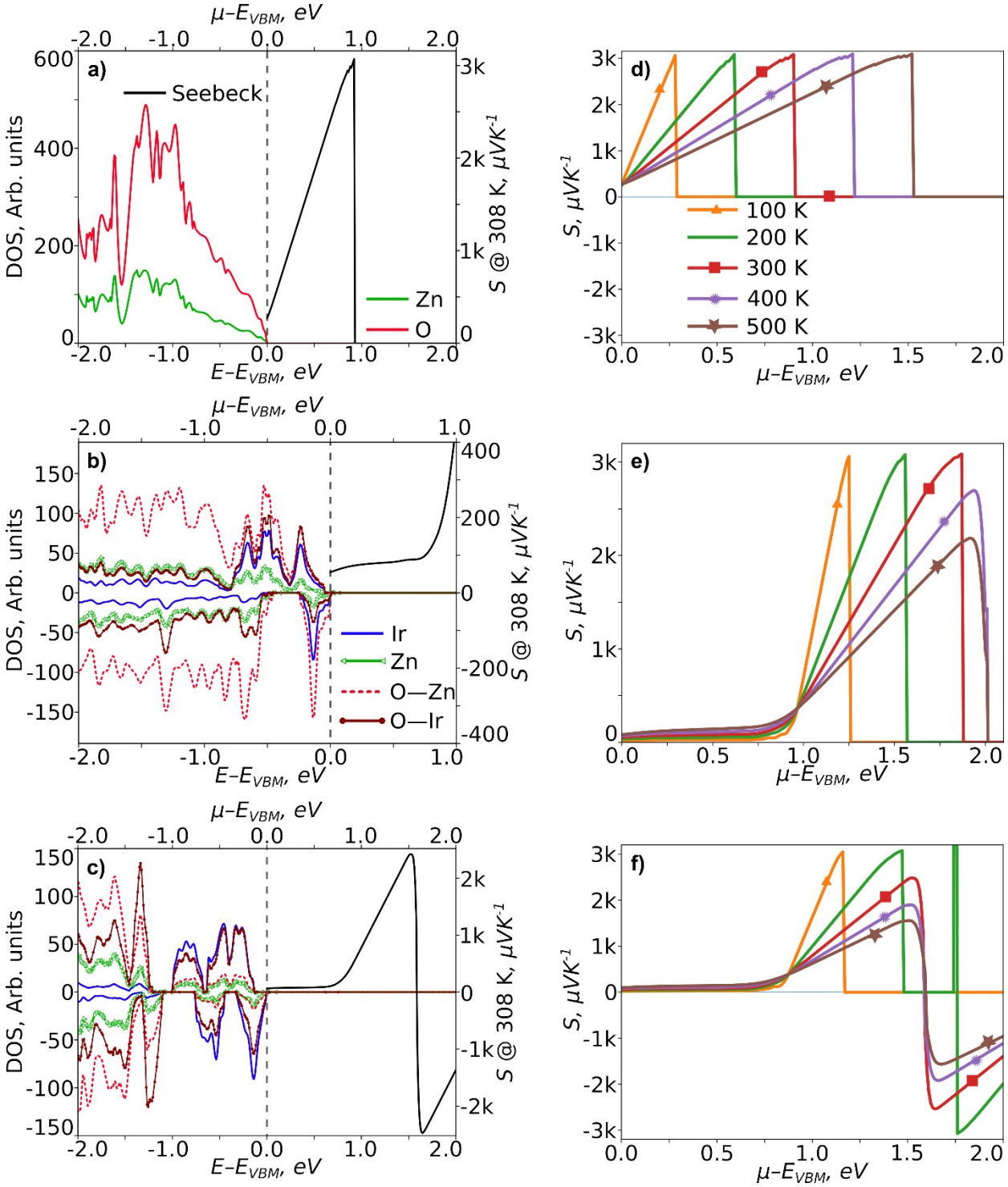

Fig. S2. Left panel: The partial DOS as a function of E- E_{VBM} (left-bottom axis) and Seebeck coefficient (S) at T=308 ^{o}K as a function of Fermi level μ_F=μ-E_{VBM} (top-right axis). The valence band maximum (E_{VBM}) is taken as zero (grey dashed line). DOS lines are smoothed with a cubic spline. No scaling is applied. Right panel: the Seebeck coefficient for a range of temperatures. a,d) ZnO; b,e) $Ir^{3+}O_4$, c, f) $Ir^{4+}O_5$.

References

[1] B.P. Pritchard, D. Altarawy, B. Didier, T.D. Gibson, and T.L. Windus, J. Chem. Inf. Model. **59**, 4814 (2019).
[2] Y. Ping, G. Galli, and W.A. Goddard, J. Phys. Chem. C **119**, 11570 (2015).
[3] D. Gryaznov, E. Blokhin, A. Sorokine, E.A. Kotomin, R.A. Evarestov, A. Bussmann-Holder, and J. Maier, J. Phys. Chem. C **117**, 13776 (2013).
[4] R.A. Evarestov, A.I. Panin, A.V. Bandura, and M.V. Losev, J. Phys.: Conf. Ser. **117**, 012015 (2008).
[5] H. Sowa and H. Ahsbahs, J Appl Cryst **39**, 169 (2006).
[6] A. Janotti and C.G. Van de Walle, Rep. Prog. Phys. **72**, 126501 (2009).
[7] A.A. Bolzan, C. Fong, B.J. Kennedy, and C.J. Howard, Acta Crystallogr. Sect. B **53**, 373 (1997).
[8] T. Arikawa, Y. Takasu, Y. Murakami, K. Asakura, and Y. Iwasawa, J Phys Chem B **102**, 3736 (1998).
[9] M.-S. Miao and R. Seshadri, J Phys Condens Matter **24**, 215503 (2012).
[10] M. Dekkers, G. Rijnders, and D.H.A. Blank, Applied Physics Letters **90**, 021903 (2007).
[11] M.J. Wahila, Z.W. Lebens-Higgins, A.J. Jackson, D.O. Scanlon, T.-L. Lee, J. Zhang, K.H.L. Zhang, and L.F.J. Piper, Phys Rev B **100**, (2019).