Electronic Supplementary Information

Influence of alkali metal ions on the defect induced photoluminescence properties of double tungstate compounds $ACe(WO_4)_2$ (A = Li, Na, K): Experimental and *ab initio* theoretical study

Nibedita Haldar[(a)*] and Tanmoy Mondal[(b)]

[(a)*]Institute of Engineering and Management (IEM), University of Engineering and Management Kolkata, 700160, India

[(b)]School of Materials Science and Nanotechnology, Jadavpur University, Jadavpur, Kolkata – 700032, India

[(*)] Corresponding author's email ID: nibedita.haldar@uem.edu.in, Tel: 8250478156

Table S1. Coordination environment of triclinic ACWO nanostructures.

Coordinates atoms	x	y	z	Occupancy	Site occupancy	symmetry
Li1/Na1/K1	0.2815	0.7733	0.1567	1.0	1a	1
Li2/Na2/K2	0.7184	0.2266	0.8432	1.0	1a	1
Ce1	0.1740	0.2878	0.4547	1.0	1a	1
Ce2	0.2860	0.7121	0.5452	1.0	1a	1
O1	0.1823	0.3500	0.7987	1.0	1a	1
O2	0.8176	0.6500	0.2012	1.0	1a	1
O3	0.4619	0.6413	0.2627	1.0	1a	1
O4	0.5380	0.4586	0.7372	1.0	1a	1
O5	0.8659	0.0119	0.1955	1.0	1a	1
O6	0.1340	0.9880	0.8044	1.0	1a	1
O7	0.7074	0.0107	0.4898	1.0	1a	1
O8	0.2925	0.9893	0.5101	1.0	1a	1
O9	0.1740	0.6339	0.5530	1.0	1a	1

O10	0.8259	0.3660	0.4469	1.0	1a	1
O11	0.4847	0.8316	0.0074	1.0	1a	1
O12	0.5152	0.1683	0.9925	1.0	1a	1
O13	0.0578	0.3132	0.1062	1.0	1a	1
O14	0.9421	0.6868	0.8937	1.0	1a	1
O15	0.3906	0.1712	0.2675	1.0	1a	1
O16	0.6093	0.8287	0.7324	1.0	1a	1
W1	0.2753	0.2990	0.0396	1.0	1a	1
W2	0.7246	0.7009	0.9603	1.0	1a	1
W3	0.6569	0.1086	0.2887	1.0	1a	1
W4	0.3430	0.8913	0.7112	1.0	1a	1

Table S2. Refined structural parameters and the reliability factors from Rietveld refinement of ACWO nanostructures.

Properties		**LCWO**	**NCWO**	**KCWO**
Lattice parameter (A^0)	a	7.082(7)	7.499(5)	7.061(4)
	b	8.009(10)	8.254(6)	8.011(5)
	c	7.405(8)	7.058(5)	7.445(4)
	α	114.341	113.441	114.122
	β	116.476	115.151	116.991
	γ	90.258	91.462	90.285
Unit cell volume $(A^0)^3$		333.343(6)	352.753(4)	333.032(3)
Bond length (A^0)	A-O	2.413(4)	2.503(4)	2.408(2)
	Ce-O	2.410(18), 2.569(14)	2.521(14), 2.636(12)	2.394(10), 2.590(7)
	W-O	1.919(4)	1.978(4)	1.916(5)
Bond angle (in degree)	A-O-W	92.280(3)	93.269(18)	92.541(12)
	A-O-Ce	114.613(19)	114.606(17)	114.334(11)
	O-Ce-O	74.790(3)	74.800(7)	74.650(13)
	Ce-O-W	145.346(18)	145.402(3)	145.208(8)
	O-A-O	69.283(3)	66.861(4)	69.272(12)
	O-W-O	89.614(13)	87.290(5)	89.600(5)
R_p (%)		10.5	12.8	13.9
R_{wp} (%)		15.5	16.2	17.3
R_{exp} (%)		10.2	10.3	10.3
χ^2		2.80	2.51	2.82

Table S3. The details of the deconvolution of the FTIR bands of ACWO nanostructures.

Samples	Peak position (cm^{-1})		Area (cm^2)	FWHM	χ^2
LCWO	660 – 718	670	0.097	1.761	2.10
		679	0.052	6.188	
		695	0.203	11.938	
		702	0.065	4.608	
	718-780	742	0.926	14.634	2.30
		762	1.179	15.532	
	780 – 910	812	5.781	29.355	2.70
		857	12.933	46.013	
		882	4.594	29.232	
NCWO	660 – 718	670	0.061	1.347	2.22
		678	0.094	9.493	
		693	0.021	4.076	
		697	0.164	15.086	
	718-780	733	0.695	14.939	3.20
		747	1.619	27.337	
	780 – 910	797	1.795	21.575	2.42
		823	3.520	35.468	
		867	11.595	53.496	
KCWO	660 – 718	670	0.048	1.323	3.70
		681	0.175	10.116	
		696	0.108	7.053	
		706	0.071	8.035	

	718-780	740	0.264	11.615	3.40
		764	0.220	11.566	
	780 – 910	816	4.412	34.078	1.97
		856	11.339	43.998	
		882	2.626	25.473	

Table S4. Lattice parameters of ACWO nanostructures from DFT calculation.

Lattice parameter (Å)	LCWO	NCWO	KCWO
a	7.110	7.115	7.760
b	7.430	7.348	7.571
c	7.535	7.271	7.577
A-O	2.06	2.32	2.79
Ce-O	2.45	2.38	2.35
W-O	1.82	1.80	1.82

Table S5. The contributed orbitals for different emissions of ACWO nanostructures from defect states (DFT).

Transitions	LCWO	NCWO	KCWO	Deformed structure of CeO_8
Blue II ($2V_O$)	$5d_{xz} \rightarrow 4f$	$5d_{xz} \rightarrow 4f$	$5d_{xz} \rightarrow 4f$	CeO_6
Blue III (V_O)	$(5d_{xz}, 5d_{x^2-y^2}) \rightarrow 4f$	$(5d_{xz}, 5d_{x^2-y^2}) \rightarrow 4f$	$(5d_{xy}, 5d_{yz}) \rightarrow 4f$	CeO_7
Green ($2V_O$)	$5d_{x^2-y^2} \rightarrow 4f$	$5d_{x^2-y^2} \rightarrow 4f$	$5d_{x^2-y^2} \rightarrow 4f$	CeO_6

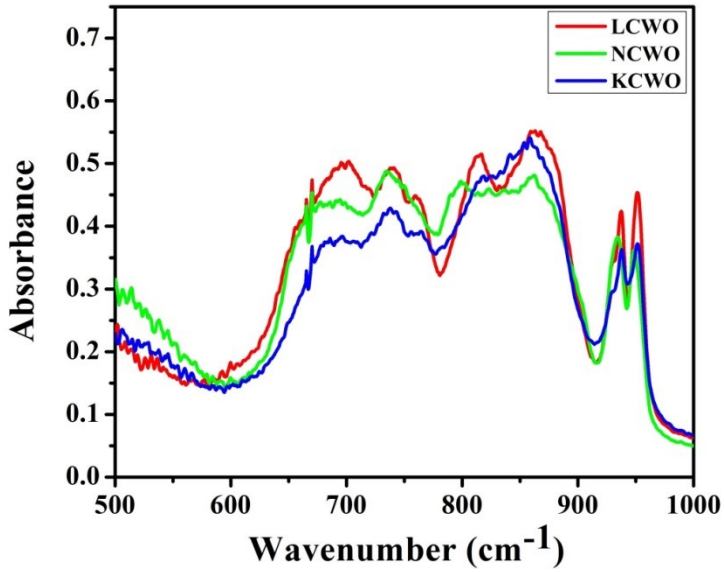

Fig. S1 FTIR of ACWO nanostructures.

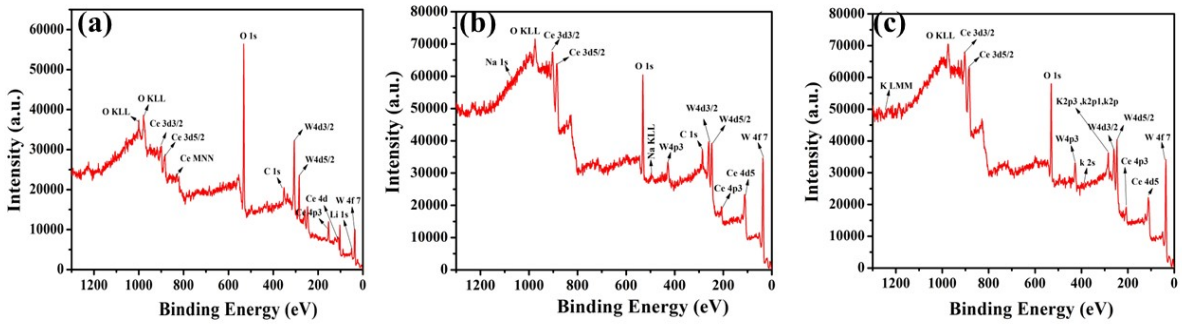

Fig. S2 XPS wide spectrum of (a)LCWO, (b)NCWO and (c)KCWO respectively.

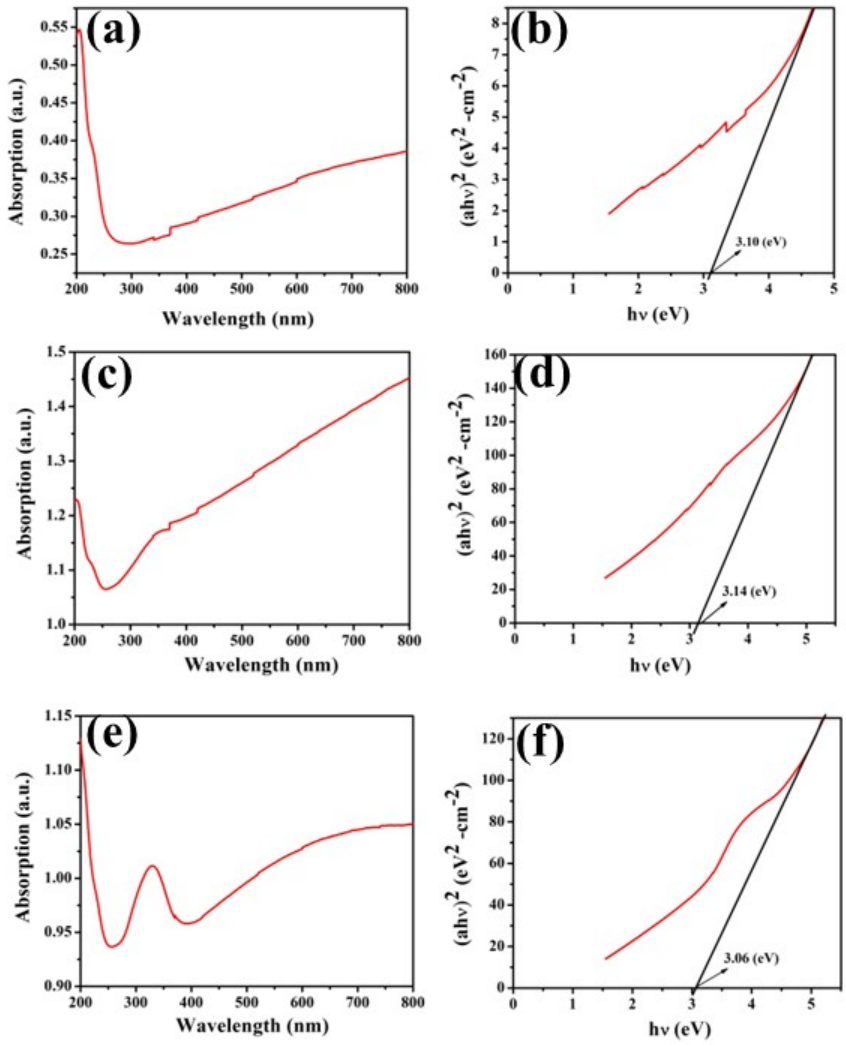

Fig. S3 UV spectra and corresponding band gaps for (a, b) LCWO, (c, d) NCWO and (e, f) KCWO respectively.

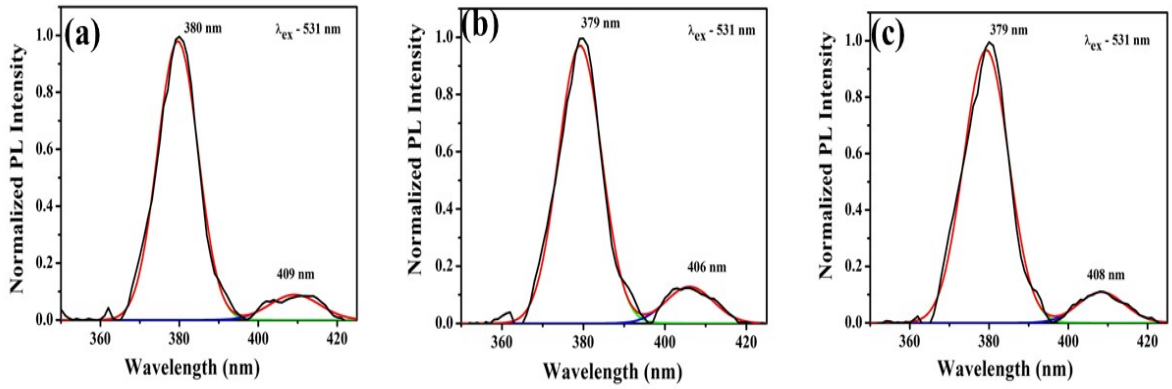

Fig. S4 PLE spectra for (a)LCWO, (b)NCWO and (c)KCWO respectively.

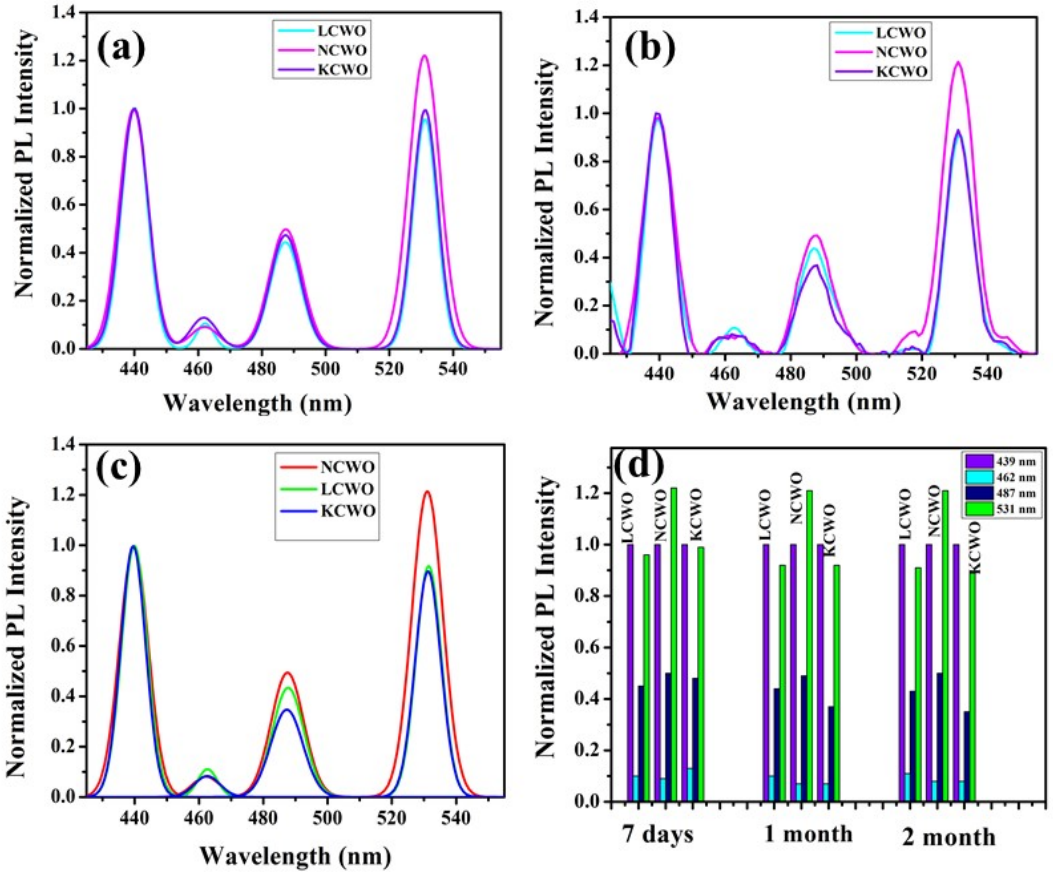

Fig. S5 (a-c) Photoluminescence spectra of ACWO samples after 7 days, 1 month and 2 months from the preparation date and (d) stability curve of the fluorescence experiments.

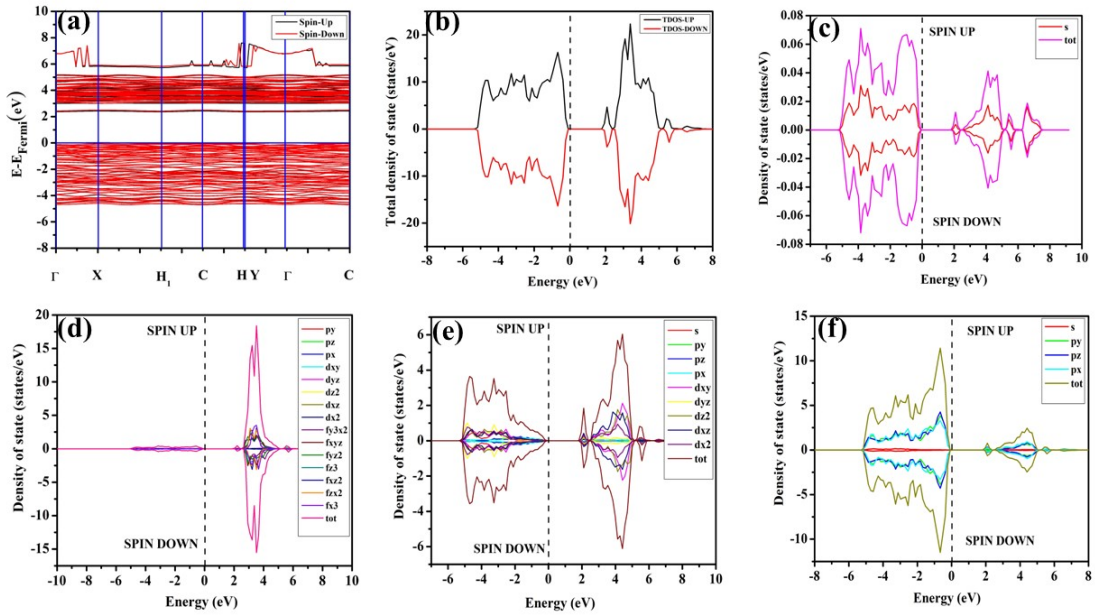

Fig. S6 (a) Band structure and (b) spin polarised TDOS and PDOS of (c) Li, (d) Ce, (e) W and (f) O of LCWO – $V_O^{\bullet}$.

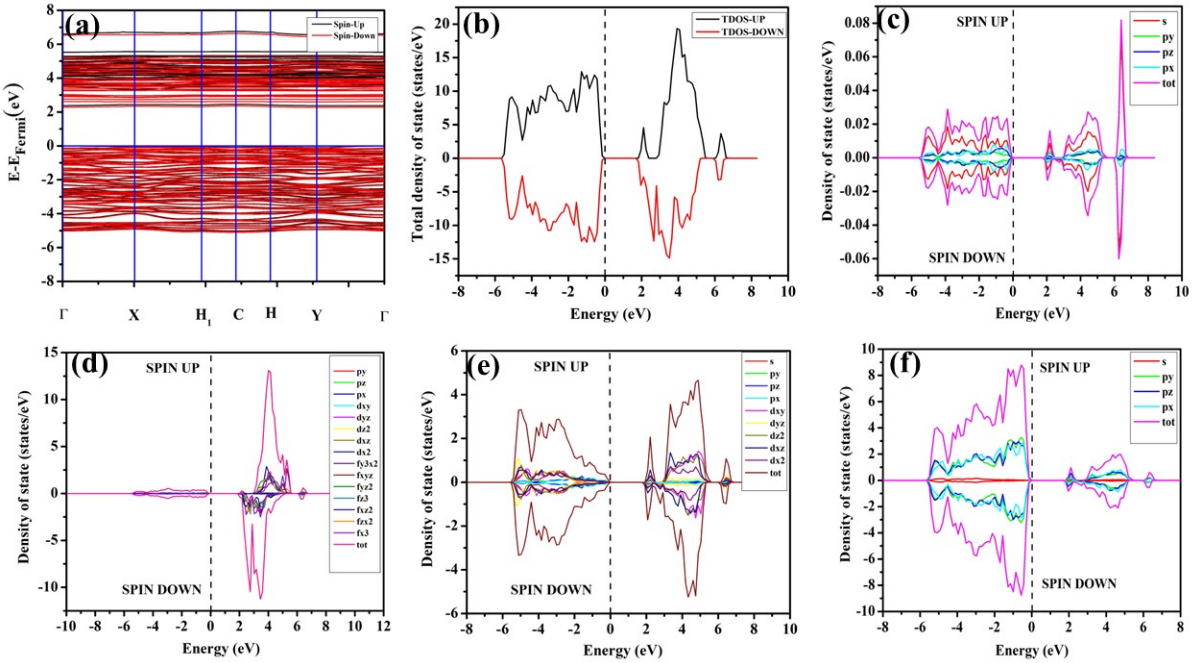

Fig. S7 (a) Band structure and (b) spin polarised TDOS and PDOS of (c) Na, (d) Ce, (e) W and (f) O of NCWO – $V_O^{\bullet}$.

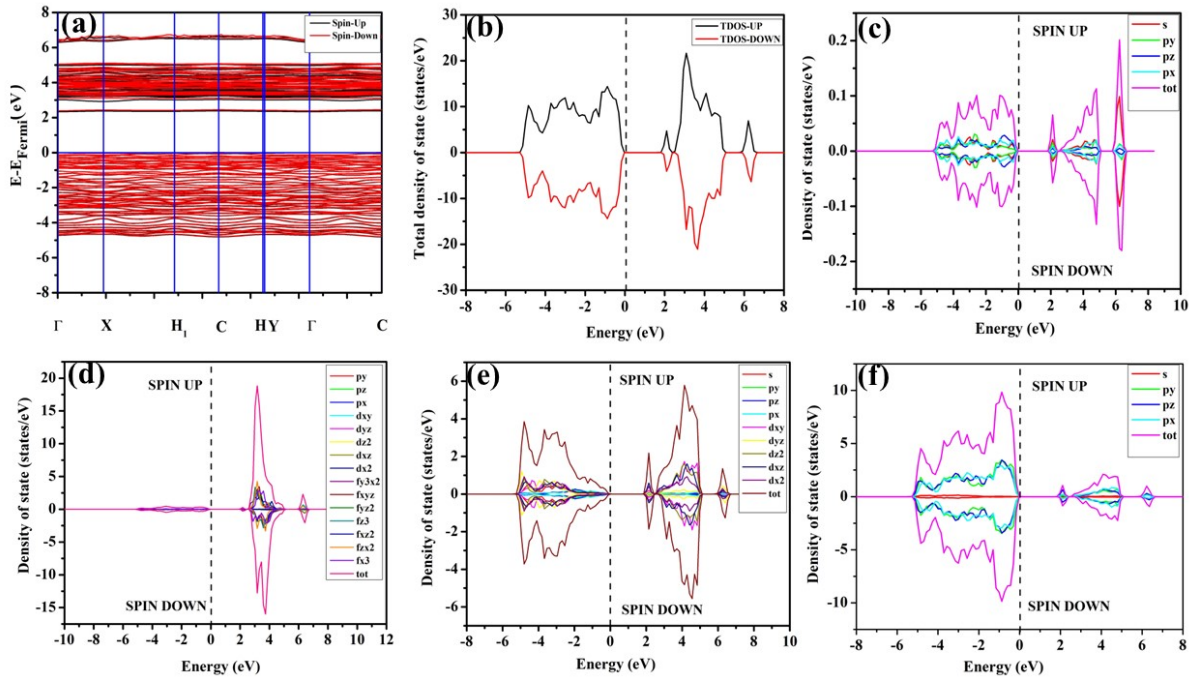

Fig. S8 (a) Band structure and (b) spin polarised TDOS and PDOS of (c) K, (d) Ce, (e) W and (f) O of KCWO – $V_O^{\bullet}$.

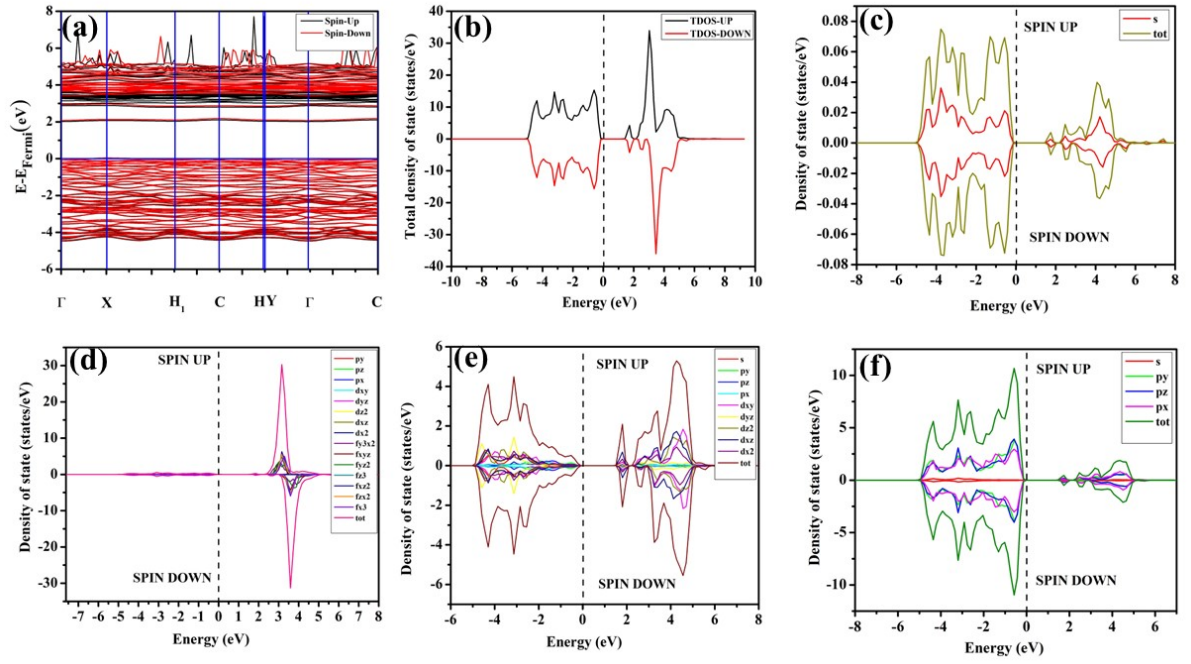

Fig. S9 (a) Band structure and (b) spin polarised TDOS and PDOS of (c) Li, (d) Ce, (e) W and (f) O of LCWO – $2V_O^{\bullet}$.

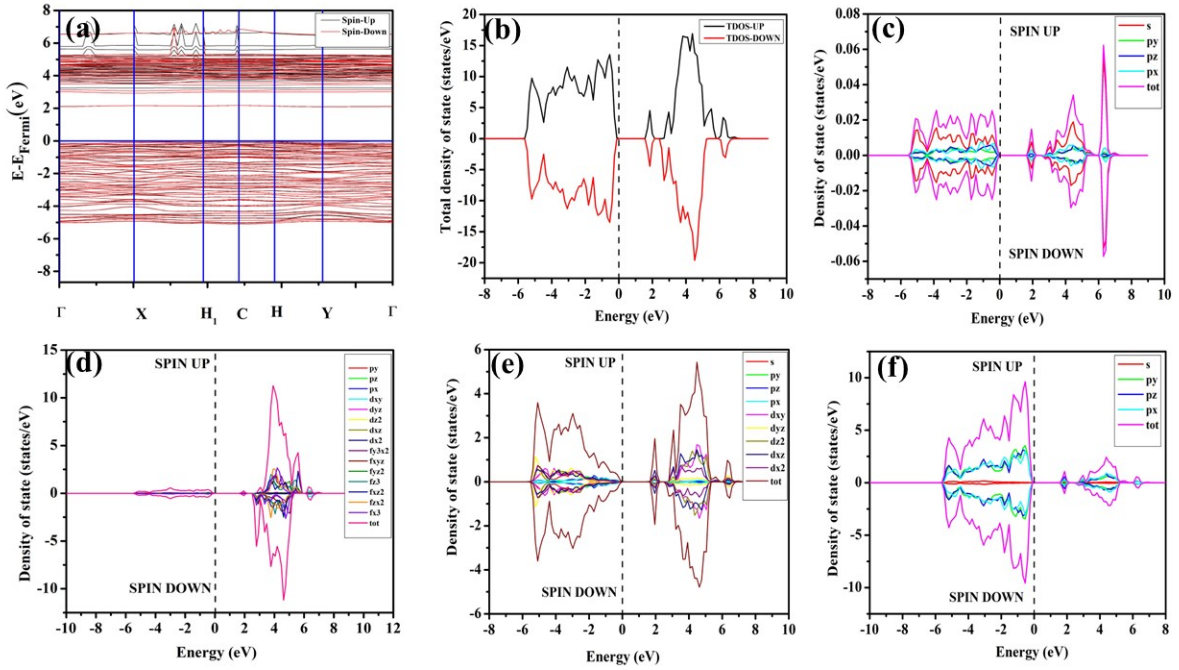

Fig. S10 (a) Band structure and (b) spin polarised TDOS and PDOS of (c) Na, (d) Ce, (e) W and (f) O of NCWO – $2V_O^{\bullet}$.

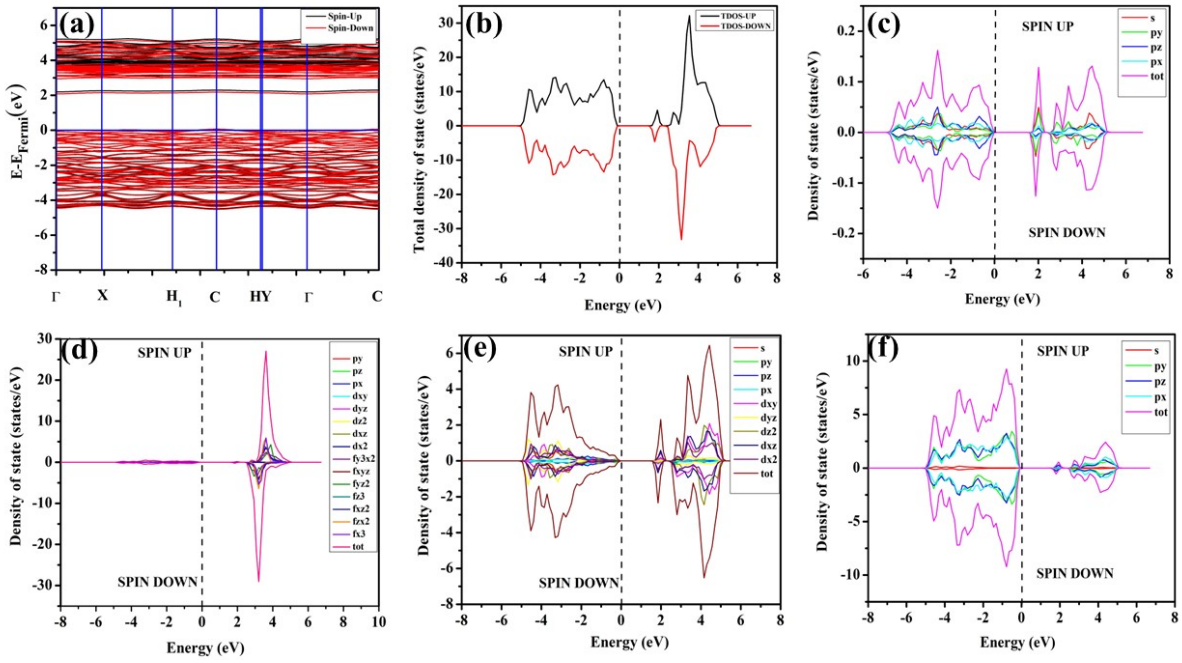

Fig. S11 (a) Band structure and (b) spin polarised TDOS and PDOS of (c) K, (d) Ce, (e) W and (f) O of KCWO – $2V_O^{\bullet}$.