Synthesis, Crystal and Electronic Structures, Linear and Nonlinear Optical Properties of Oxyhalides CeHaVIO$_4$(Ha=Cl, Br; VI=Mo, W)

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Table S1. Atomic coordinate parameters for $CeClMoO_4$, $CeClWO_4$, $CeBrMoO_4$, and $CeBrWO_4$.

Atom	Wyckoff	x	y	z	Occupancy	U_{eq} (Å^2)
CeClMoO$_4$						
Ce1	2a	0.49975(3)	0.45044(5)	0.76321(2)	1	0.00708(8)
Ce2	2a	0.91378(3)	0.04967(5)	1.01256(2)	1	0.00692(8)
Mo1	2a	0.06463(5)	0.50589(5)	0.72930(5)	1	0.00512(8)
Mo2	2a	0.34954(5)	0.00201(6)	0.97764(5)	1	0.00599(9)
Cl1	2a	0.68372(17)	1.0092(6)	0.76515(17)	1	0.0135(3)
Cl2	2a	0.73163(19)	0.4896(6)	1.01397(16)	1	0.0125(3)
O1	2a	0.4387(4)	0.2634(5)	1.0444(5)	1	0.0123(7)
O2	2a	0.4444(4)	0.7286(5)	0.9888(6)	1	0.0118(7)
O3	2a	-0.0265(4)	0.7610(4)	0.7927(5)	1	0.0081(6)
O4	2a	-0.0213(4)	0.2304(4)	0.7380(5)	1	0.0069(6)
O5	2a	0.1692(4)	-0.0269(6)	1.0117(4)	1	0.0095(6)
O6	2a	0.2427(4)	0.4984(8)	0.7722(4)	1	0.0100(6)
O7	2a	0.3673(5)	0.0702(6)	0.7612(4)	1	0.0135(9)
O8	2a	0.0570(5)	0.5609(5)	0.5111(3)	1	0.0074(7)
CeClWO$_4$						
Ce1	2a	0.74728(5)	0.94769(18)	0.16606(15)	1	0.0073(3)
Ce2	2a	0.24731(5)	0.94579(18)	0.42028(16)	1	0.0073(3)
Ce3	2a	0.96537(3)	0.9986(2)	0.25194(9)	1	0.00419(16)
Ce4	2a	0.46558(3)	1.0029(3)	0.55740(10)	1	0.00432(15)
W1	2a	0.82105(4)	0.5030(3)	0.42716(10)	1	0.00498(19)
W2	2a	0.32184(3)	0.5016(2)	0.23665(10)	1	0.00578(18)
W3	2a	0.09491(7)	1.0031(2)	0.4741(2)	1	0.0032(4)
W4	2a	0.59479(7)	0.9986(2)	0.1670(2)	1	0.0029(4)
Cl1	2a	0.6328(2)	0.9892(14)	0.3584(8)	1	0.0095(8)
Cl2	2a	0.1323(3)	0.9847(17)	0.1082(8)	1	0.0157(13)
Cl3	2a	1.1554(2)	0.5118(16)	0.3704(7)	1	0.0116(11)
Cl4	2a	0.6556(2)	0.4903(16)	0.6216(8)	1	0.0142(11)
O1	2a	0.0070(6)	0.7289(16)	0.3237(16)	1	0.006(2)
O2	2a	0.5075(5)	0.2760(18)	0.0801(18)	1	0.0049(18)
O3	2a	0.0060(6)	0.2776(15)	0.2709(15)	1	0.009(2)
O4	2a	0.7732(5)	0.7537(17)	0.4605(15)	1	0.009(2)
O5	2a	0.5065(4)	0.7298(17)	0.0163(15)	1	0.0037(16)
O6	2a	0.7742(6)	0.239(2)	0.4038(19)	1	0.013(3)

O7	2a	0.2773(5)	0.7570(18)	0.1468(15)	1	0.008(2)
O8	2a	0.4727(4)	0.9236(13)	0.2873(11)	1	0.0052(16)
O9	2a	0.9768(4)	0.9351(14)	0.0282(10)	1	0.014(5)
O10	2a	0.2732(4)	0.2338(15)	0.2119(14)	1	0.0039(15)
O11	2a	0.8130(5)	0.5435(18)	0.1982(13)	1	0.010(2)
O12	2a	0.3204(5)	0.5639(14)	0.4611(10)	1	0.0040(16)
O13	2a	0.4123(4)	0.506(2)	0.2379(14)	1	0.0078(18)
O14	2a	0.9133(5)	0.487(3)	-0.0029(19)	1	0.011(2)
O15	2a	0.3759(5)	-0.008(3)	0.4931(15)	1	0.0036(17)
O16	2a	0.8758(4)	0.028(2)	0.2370(14)	1	0.010(2)
$CeBrMoO_4$						
Ce1	2a	-0.49130(2)	0.45566(4)	-0.70036(2)	1	0.00712(6)
Ce2	2a	-0.92350(2)	0.95430(4)	-0.44924(2)	1	0.00731(6)
Mo1	2a	-0.06780(3)	0.49756(5)	-0.73530(4)	1	0.00529(7)
Mo2	2a	-0.34715(3)	0.00631(5)	-0.48516(4)	1	0.00581(7)
Br1	2a	-0.67877(5)	1.0015(2)	-0.69846(5)	1	0.01132(10)
Br2	2a	-0.73596(4)	0.4998(2)	-0.94860(5)	1	0.01129(10)
O1	2a	-0.4326(3)	0.2703(5)	-0.9718(4)	1	0.0088(6)
O2	2a	-0.4364(4)	0.7367(5)	-0.9225(4)	1	0.0091(5)
O3	2a	-0.9798(4)	0.7704(5)	-0.7211(5)	1	0.0097(6)
O4	2a	-0.9833(4)	0.2366(5)	-0.6710(4)	1	0.0109(6)
O5	2a	-0.1726(4)	-0.0018(9)	-0.4374(4)	1	0.0136(5)
O6	2a	-0.2431(3)	0.5214(6)	-0.7014(3)	1	0.0080(5)
O7	2a	-0.3583(5)	0.0633(6)	-0.7009(4)	1	0.0111(8)
O8	2a	-0.0563(5)	0.4396(6)	-0.9504(4)	1	0.0113(7)
$CeBrWO_4$						
Ce1	2a	0.49162(10)	0.45288(12)	0.69896(4)	1	0.00851(19)
Ce2	2a	0.92431(9)	0.95285(12)	0.44826(4)	1	0.00792(19)
W1	2a	0.06693(5)	0.49777(5)	0.72856(6)	1	0.00643(9)
W2	2a	0.34760(5)	0.00404(5)	0.47822(6)	1	0.00602(9)
Br1	2a	0.67902(17)	0.0016(3)	0.69697(11)	1	0.0104(3)
Br2	2a	0.73592(18)	0.4986(3)	0.94727(12)	1	0.0126(3)
O1	2a	0.4375(7)	0.2668(8)	0.9696(9)	1	0.0087(12)
O2	2a	0.4401(7)	0.7376(9)	0.9200(9)	1	0.0097(12)
O3	2a	0.9860(8)	0.7693(8)	0.2793(12)	1	0.0075(11)
O4	2a	0.9871(8)	0.2357(8)	0.6669(8)	1	0.0075(11)
O5	2a	0.1734(8)	0.9996(14)	0.4351(8)	1	0.0065(11)
O6	2a	0.2442(8)	0.5159(16)	0.7042(9)	1	0.0120(15)
O7	2a	0.3609(11)	0.0532(13)	0.7011(6)	1	0.0093(18)

O8	2a	0.0557(12)	0.4339(12)	0.9515(7)	1	0.013(2)

Table S2. Selected interatomic distances for CeClWO$_4$, CeClWO$_4$, CeBrMoO$_4$, and CeBrWO$_4$.

Atom Pairs		Distances (Å)	Atom Pairs		Distances (Å)
CeClMoO4					
Mo1	O3	1.787(3)	Ce2	Cl1	2.9579(15)
	O4	1.796(3)		Cl1	2.9965(16)
	O6	1.735(4)		Cl2	3.086(3)
	O8	1.765(3)		O3	2.485(3)
	O8	2.274(3)		O3	2.547(4)
Mo2	O1	1.817(3)		O4	2.499(4)
	O2	1.827(3)		O4	2.496(3)
	O5	1.752(4)		O5	2.479(4)
	O7	1.774(3)		O8	2.638(4)
	O7	2.299(3)			
Ce1	Cl1	3.102(3)			
	Cl2	2.9880(16)			
	Cl2	2.9923(16)			
	O1	2.552(4)			
	O2	2.472(4)			
	O2	2.469(4)			
	O6	2.472(4)			
	O7	2.540(4)			
CeClWO$_4$					
W1	O4	1.797(10)	Ce2	O7	2.576 (12)
	O6	1.798(12)		O7	2.479 (11)
	O11	1.778(11)		O10	2.472 (10)
	O11	2.169(11)		O10	2.469 (10)
	O14	1.784(10)		O12	2.654 (8)
W2	O7	1.810 (10)		O15	2.488 (9)

	O12	1.794 (8)		Cl2	2.980(5)
	O12	2.179(8)		Cl2	2.952 (6)
	O13	1.773(9)		Cl3	3.109 (8)
W3	O1	1.823 (10)	Ce3	O1	2.446(13)
	O3	1.820 (9)		O1	2.460(16)
	O9	1.842(8)		O3	2.497(18)
	O9	2.158 (8)		O3	2.499(16)
	O16	1.746 (9)		O9	2.530(3)
W4	O2	1.831 (10)		O14	2.457(10)
	O5	1.826 (10)		Cl2	3.109 (9)
	O8	2.190 (9)		Cl3	2.987 (5)
	O8	1.823 (9)		Cl3	2.964 (5)
	O15	1.730 (9)	Ce4	O2	2.448(12)
Ce1	O4	2.525 (11)		O2	2.483(14)
	O4	2.500(11)		O5	2.525 (11)
	O6	2.505 (13)		O5	2.458(11)
	O6	2.471 (15)		O8	2.536 (8)
	O11	2.696 (10)		O13	2.464(8)
	O16	2.514 (9)		Cl1	3.133(7)
	Cl1	2.948 (6)		Cl4	2.971 (5)
	Cl1	2.965 (5)		Cl4	2.985 (6)
	Cl4	3.126 (8)			
CeBrMoO4					
Mo1	O3	1.810(3)	Ce2	Br1	3.1321(5)
	O4	1.805(3)		Br1	3.1380(5)
	O6	1.741(3)		Br2	3.2172(12)
	O8	1.764(3)		O3	2.493(3)
	O8	2.320(3)		O3	2.496(3)
Mo2	O1	1.818(3)		O4	2.493(3)
	O2	1.804(3)		O4	2.5634(3)
	O5	1.750(4)		O5	2.451(4)
	O7	1.768(3)		O8	2.635(4)
	O7	2.321(3)			

Ce1	Br1	3.2167(12)			
	Br2	3.1245(5)			
	Br2	3.1433(5)			
	O1	2.499(3)			
	O1	2.499(3)			
	O2	2.480(3)			
	O6	2.457(3)			
	O7	2.628(4)			
CeBrWO4					
W1	O3	1.797(5)	Ce2	Br1	3.1393(16)
	O4	1.808(5)		Br1	3.1501(16)
	O6	1.765(8)		Br2	3.257(2)
	O8	1.814(5)		O3	2.505(7)
	O8	2.239(5)		O3	2.511(6)
W2	O1	1.835(5)		O4	2.491(6)
	O2	1.842(6)		O4	2.573(6)
	O5	1.755(7)		O5	2.478(8)
	O7	1.798(5)		O8	2.633(9)
	O7	2.230(5)			
Ce1	Br1	3.2514(18)			
	Br2	3.2514(18)			
	Br2	3.1466(17)			
	O1	2.474(7)			
	O2	2.521(6)			
	O2	2.486(6)			
	O2	2.537(7)			
	O6	2.473(8)			
	O7	2.697(9)			

Table S3. A summary of crystal structure and physical properties of reported compounds within the $REHaVIO_4$ (Ha=Cl, Br; RE= La-Lu; VI=Mo, W) system.

Compounds	Space Group	Unit cell parameters	Structure Type	Physical Properties	Basic building units	Refe renc

						e
LaClMoO$_4$	$P2_1/c$	19.2055(18) ×5.8046(5) ×8.0382(7) β=90.040(6) ° monoclinic V=896.10Å³	CeClWO$_4$		[LaO$_6$Cl$_3$] [MoO$_5$]	1
CeClMoO$_4$	$P2_1/c$	19.1228(18) ×5.7992(5) ×7.9591(7) β=90.037(6) ° monoclinic V= 882.64 Å³	CeClMoO$_4$	Paramagnetic, absence of any significant long range order even at 1.8 K.	[CeO$_6$Cl$_3$] [MoO$_5$]	1
NdClMoO$_4$	$Pbam$	19.9161(9) ×6.9379(3) ×7.4253(3) orthorhombic V= 1026.00 Å³	NdClMoO$_4$		[NdO$_6$Cl$_2$] [MoO$_4$]	2
YbClMoO$_4$	$C12/m$	10.1019(5) ×7.1334(3) ×6.7756(3) β= 107.408(2) ° monoclinic V=465.89Å³	YbClMoO$_4$		[YbO$_6$Cl$_2$] [MoO$_4$]	3
LaClWO$_4$	$Pbc2_1$	5.893(3) ×7.856(4) ×19.270(9) orthorhombic V= 892.11 Å³	LaClWO$_4$	Eg=4.0(2) eV (La$_{0.98}$Sm$_{0.02}$)ClWO$_4$: $^4G_{7/2}$ ->$^6H_{9/2}$, $^4G_{5/2}$ ->$^6H_{7/2}$ excited by 404 nm. (La$_{0.99}$Eu$_{0.01}$)ClWO$_4$: $^5D_0$ ->$^7F_1$, $^5D_0$ ->$^7F_2$, excited by 394 nm. (La$_{0.995}$Tb$_{0.005}$)ClWO$_4$: $^5D_4$ ->$^7F_6$, $^5D_4$ to $^7F_5$ excited by 320 nm.	[LaO$_6$Cl$_3$] [MoO$_5$]	4
LaClWO$_4$	$Pmcn$	5.893(3) ×3.928(2) × 19.270(9) orthorhombic V= 446.06 Å³	LaClWO$_4$		[LaO$_5$Cl$_4$] [MoO$_5$]	4
LaBrMoO$_4$	$P1c1$	9.8197(4) × 5.8183(2) × 8.1051(3) β=90.039(3) ° monoclinic V=463.08Å³	LaBrMoO$_4$		[LaO$_6$Br$_3$] [MoO$_5$]	5
CeBrMoO$_4$	$P1c1$	9.7691(4) ×5.8146(2) × 8.0259(3) β=90.004(3) ° monoclinic V=455.90Å³	LaBrMoO$_4$		[CeO$_6$Br$_3$] [MoO$_5$]	5
CeClMoO$_4$	$P1c1$	9.55130(10)× 5.793× 7.94950(10) β=90.0140(7) ° monoclinic		E$_g$=2.9 (1) eV	[CeO$_6$Cl$_3$] [MoO$_5$]	Th is w or

		V=439.851(7) Å³				k
CeClWO$_4$	$P1c1$	19.6059(2) 5.89450(10) 7.80090(10) β=101.4746(8)° monoclinic V=883.51(2) Å³		E$_g$=3.1 (1) eV	[CeO$_6$Cl$_3$] [MoO$_5$]	This work
CeBrMoO$_4$	$P1c1$	9.77750(10)× 5.82090(10) × 8.03220(10) β=90.0106° monoclinic V=457.143(11)Å³		E$_g$=2.8 (1) eV	[CeO$_6$Br$_3$] [MoO$_5$]	This work
CeBrWO$_4$	$P1c1$	9.87830(10)× 5.92230(10) × 7.93940(10) β=90.0083° monoclinic V=464.473(11)Å³		E$_g$=3.0 (1) eV	[CeO$_6$Br$_3$] [WO$_5$]	This work
LuBrWO$_4$	P -1	5.9292(3) ×7.1869(4) ×6.8443(4) α=93.637(3)° β=102.944(3)° γ=121.875(3)° triclinic V= 235.49Å³	LuBrWO$_4$		[LuO$_6$Br] [LuO$_4$Br$_3$] [WO$_4$]	6
TmClWO$_4$	P -1	5.9638(3) × 7.2110(4) ×6.8551(4) α=93.243(3)° β=103.066(3)° γ=121.995(3)° triclinic V= 237.93Å³	LuClMoO$_4$		[TmO$_5$Cl$_2$] [WO$_4$]	7
YbClWO$_4$	P -1	5.9235(3) ×7.1845(4) ×6.8448(4) α=93.523(3)° β=103.001(3)° γ=121.745(3)° triclinic V= 235.61Å³	LuClMoO$_4$	E$_g$=4.23 eV	[YbO$_5$Cl$_2$] [WO$_4$]	7
LuClWO$_4$	P -1	5.9292(3) × 7.1869(4) × 6.8443(4) α=93.637(3)° β=102.944(3)	LuClMoO$_4$	LuClWO$_4$:Eu^{3+}:^{5}D$_0$ ->^{7}F$_2$ to ^{7}F$_1$	[LuO$_5$Cl$_2$] [WO$_4$]	7

		$\gamma=121.875(3)$ ° triclinic V= 235.48 Å³				
LuClMoO$_4$	$P\,$-1	5.9142(2) ×7.1619(3) × 6.8144(3) $\alpha=93.724(2)$ ° $\beta=102.463(2)$ ° $\gamma=122.134(2)$ ° triclinic V=232.95 Å³	LuClMoO$_4$		[LuO$_5$Cl$_2$] [MoO$_4$]	3
SmClMoO$_4$	$C12/m1$	10.3480(5) ×7.3602(3) × 6.9084(3) $\beta=106.677(2)$ ° monoclinic V= 504.04 Å³	GdClWO$_4$		[SmO$_6$Cl$_2$] [MoO$_4$]	3
EuClMoO$_4$	$C12/m1$	10.3161(5) × 7.3280(3) × 6.8878(3) $\beta=106.773(2)$ ° monoclinic V= 498.54 Å³	GdClWO$_4$	$^5D_0 \to ^7F_0$ to $^7F_4$ emissions of Eu^{3+} in the visible region	[EuO$_6$Cl$_2$] [MoO$_4$]	3
GdClMoO$_4$	$C12/m1$	10.2890(5) ×7.3051(3) ×6.8711(3) $\beta= 106.864(2)$ ° monoclinic V= 494.24Å³	GdClWO$_4$	GdCl[MoO$_4$] is a close-to-ideal paramagnet with no hint to magnetic interactions down to 1.8 K.	[GdO$_6$Cl$_2$] [MoO$_4$]	3
TbClMoO$_4$	$C12/m1$	10.2517(5) ×7.2682(3) × 6.8497(3) $\beta=106.963(2)$ ° monoclinic V= 488.18 Å³	GdClWO$_4$	$^5D_4 \to ^7F_0$ to $^7F_6$ transitions of Tb^{3+} in the visible region	[TbO$_6$Cl$_2$] [MoO$_4$]	3
DyClMoO$_4$	$C12/m1$	10.2199(5) ×7.2367(3) × 6.8322(3) $\beta=107.057(2)$ ° monoclinic V= 483.07 Å³	GdClWO$_4$	Paramagnet, absence of any long range order down to 1.8 K.	[DyO$_6$Cl$_2$] [MoO$_4$]	3
HoClMoO$_4$	$C12/m1$	10.1900(5) ×7.2147(3) ×6.8148(3) $\beta=107.142(2)$ ° V= 478.75 Å³	GdClWO$_4$		[HoO$_6$Cl$_2$] [MoO$_4$]	3
ErClMoO$_4$	$C12/m1$	10.1536(5) ×7.1874(3)	GdClWO$_4$		[ErO$_6$Cl$_2$] [MoO$_4$]	3

		× 6.7964(3) β=107.236(2)° monoclinic V= 473.71 Å³				
TmClMoO$_4$	$C12/m1$	10.1327(5) ×7.1591(3) × 6.7850(3) β=107.320(2)° monoclinic V=469.87 Å³	GdClWO$_4$		[TmO$_6$Cl$_2$] [MoO$_4$]	3
GdClWO$_4$	$C12/m1$	10.3219(5) ×7.3249(3) × 6.8888(3) β=107.229(2)° monoclinic V= 497.46 Å³	GdClWO$_4$	GdClWO$_4$:Eu^{3+}:^{5}D$_0$ ->^{7}F$_2$ to ^{7}F$_1$		2, 7
TbClWO$_4$	$C12/m1$	10.2806(5) × 7.2858(3) × 6.8713(3) β=107.293(2)° monoclinic V= 491.41Å³	GdClWO$_4$	^{5}D$_4$ ->^{7}F$_5$ to ^{7}F$_6$ emissions of Tb^{3+} in the visible region E$_g$=4.24 eV		7
DyClWO$_4$	$C12/m1$	10.2524(5) × 7.2583(3) × 6.8561(3) β= 107.401(2)° monoclinic V= 486.84Å³	GdClWO$_4$			7
HoClWO$_4$	$C12/m1$	10.2154(5) × 7.2303(3) × 6.8333(3) β= 107.470(2)° monoclinic V= 481.43Å³	GdClWO$_4$			7
ErClWO$_4$	$C12/m1$	10.1877(5) × 7.2053(3) ×6.8201(3) β= 107.561(2)° monoclinic V= 477.30Å³	GdClWO$_4$			7
PrBrMoO$_4$	P -1	6.9795(2) × 7.4069(2) × 11.2088(4) α= 105.945(2) ° β= 106.702(2)° γ= 92.355(2) ° triclinic V= 92.355(2)Å³	YbBrMoO$_4$		[PrO$_4$Br$_3$] [PrO$_6$Br] [MoO$_4$]	8
NdBrMoO$_4$	P -1	6.9529(2)	YbBrMoO$_4$		[NdO$_4$Br$_3$]	8

		×7.3756(2) ×11.1770(4) α= 106.061(2) ° β= 106.743(2) ° γ= 92.329(2) ° triclinic V= 522.92Å³			[NdO$_6$Br] [MoO$_4$]	
SmBrMoO$_4$	*P* -1	6.9138(2) ×7.3078(2) ×11.1045(4) α= 106.061(2) ° β= 106.983(2) ° γ= 92.239(2) ° triclinic V= 511.24Å³	YbBrMoO$_4$		[SmO$_4$Br$_3$] [SmO$_6$Br] [MoO$_4$]	8
GdBrMoO$_4$	*P* -1	6.8853(2) × 7.2628(2) ×11.0593(4) α= 106.142(2) ° β= 107.098(2) ° γ= 92.260(2) ° triclinic V= 503.31Å³	YbBrMoO$_4$		[GdO$_4$Br$_3$] [GdO$_6$Br] [MoO$_4$]	8
TbBrMoO$_4$	*P* -1	6.8664(2) × 7.2206(2) ×10.9705(4) α= 105.574(2) ° β= 107.262(2) ° γ= 92.516(2) ° triclinic V= 495.81Å³	YbBrMoO$_4$		[TbO$_4$Br$_3$] [TbO$_6$Br] [MoO$_4$]	8
DyBrMoO$_4$	*P* -1	6.8565(2) × 7.1913(2) ×10.9319(4) α= 105.397(2) ° β=107.332(2) ° γ= 92.750(2) ° triclinic V= 491.33Å³	YbBrMoO$_4$		[DyO$_4$Br$_3$] [DyO$_6$Br] [MoO$_4$]	8
HoBrMoO$_4$	*P* -1	6.8516(2) ×7.1793(2) ×10.8832(4) α= 105.0310(10) ° β=107.3420(10) ° γ=	YbBrMoO$_4$		[HoO$_4$Br$_3$] [HoO$_6$Br] [MoO$_4$]	8

		93.1450(10) ° triclinic V= 488.42Å³				
ErBrMoO$_4$	P -1	6.8481(2) ×7.1600(2) ×10.8135(4) α= 104.4300(10) ° β=107.4550(10) ° γ= 93.6640(10) ° triclinic V= 484.29Å³	YbBrMoO$_4$		[ErO$_4$Br$_3$] [ErO$_6$Br] [MoO$_4$]	8
TmBrMoO$_4$	P -1	6.8610(2) × 7.1504(2) ×10.7455(4) α= 103.613(2) ° β=107.627(2) ° γ= 94.238(2) ° triclinic V= 482.26 Å³	YbBrMoO$_4$		[TmO$_4$Br$_3$] [TmO$_6$Br] [MoO$_4$]	8
YbBrMoO$_4$	P -1	6.8600(2) × 7.1324(2) ×10.6973(4) α= 103.2340(10) ° β=107.6650(10) ° γ= 94.7120(10) ° triclinic V= 478.95 Å³	YbBrMoO$_4$		[YbO$_4$Br$_3$] [YbO$_6$Br] [MoO$_4$]	8
LuBrMoO$_4$	P -1	6.8594(2) ×7.1270(2) ×10.6618(4) α=102.954(2) ° β=107.688(2) ° γ=95.034(2) ° triclinic V= 477.08 Å³	YbBrMoO$_4$		[LuO$_4$Br$_3$] [LuO$_6$Br] [MoO$_4$]	8
GdBrWO$_4$	P -1	6.9118(4) × 7.2772(4) ×11.0647(6) α=105.518(4) ° β=107.514(4) ° γ=92.650(4) ° triclinic V= 506.50 Å³	YbBrMoO$_4$			9
TbBrWO$_4$	P -1	6.9050(4) ×	YbBrMoO$_4$			9

		7.2425(4) ×10.9718(6) α=104.663(4)° β=107.754(4)° γ=93.058(4)° triclinic V= 500.44 Å³				
DyBrWO$_4$	P -1	6.8970(4) ×7.2193(4) ×10.9266(6) α=104.366(4)° β=107.811(4)° γ=93.460(4)° triclinic V= 496.27 Å³	YbBrMoO$_4$			9
ErBrWO$_4$	P -1	6.8976(4) ×7.1902(4) ×10.8208(6) α=103.365(4)° β=107.994(4)° γ=94.347(4)° triclinic V= 490.26 Å³	YbBrMoO$_4$			9
HoBrWO$_4$	P -1	6.8957(4) × 7.2050(4) ×10.8732(6) α=103.885(4)° β=107.892(4)° γ=93.915(4)° triclinic V= 493.13 Å³	YbBrMoO$_4$	without any magnetic ordering above 60 K		9
TmBrWO$_4$	P -1	6.8927(3) ×7.1725(4) ×10.7748(6) α=102.922(4)° β=108.122(4)° γ=94.577(4)° triclinic V= 486.98 Å³	YbBrMoO$_4$			9
YbBrWO$_4$	P -1	6.8857(4) ×7.1496(4) ×10.7432(6) α=102.715(4)° β=108.201(4)° γ=94.859(4)° triclinic	YbBrMoO$_4$			9

	V= 483.33 Å³				

Table S4. Comparison of photocurrent density between $CeHaVIO_4$ (Ha=Cl, Br, VI=Mo, W) compounds and selected reported compounds.

Compounds	Current Density ($\mu A/cm^2$)	Reference
$Rb_2Ba_3Cu_2Sb_2S_{10}$	0.006	10
$Pb_5Sn_3S_{10}Cl_2$	0.019	11
$RbIn_4S_6Cl$	0.029	11
$BaCuSbSe_3$	0.03	12
$BaCuSbS_3$	0.055	12
$Sr_6Cd_2Sb_6S_{10}O_7$	0.065	13
$Eu_3Gd_6MgS_2B_{20}O_{41}$	0.12	14
$CeBrWO_4$	0.1615	This work
$LaNi_{0.8}Fe_{0.2}O_3$	0.25	15
$CeBrMoO_4$	0.3321	This work
$Cs2CuBr_4$	0.5	16
$CeClWO_4$	0.5527	This work
$CeClMoO_4$	0.747	This work
$Eu_8In_{17.33}S3_4$	1	17
$Tm_4S_4Te_3$	1.1	18
$Eu_{5.4}Sm_{3.6}MgS_2B_{20}O_{41}$	1.62	14
$Zn_4B_6O_{12}S$	2.1	19
$Ho_4S_4Te_3$	2.2	18
$Gd_4S_4Te_3$	2.3	18
Sr_2YbRuO_6	5.5	20
$Rb_2CuSb_7S_{12}$	10	21
$Ba_3HgGa_2S_7$	12.2	22
$La_{2.1}Bi_{2.9}Ti_2O_{11}Cl$	15	23
Ba_2ZnSe_3	25	24
$BaAu_2S_2$	30	25
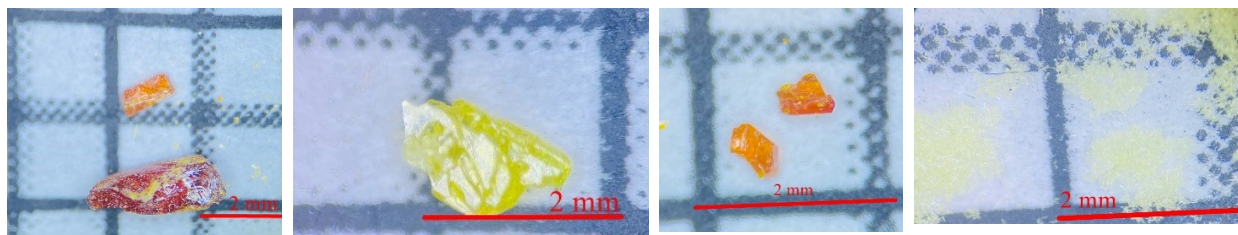
Figure S1. The optical microscope images of crystals of $CeHaVIO_4$ (Ha=Cl, Br; VI=Mo, W), from left to right: $CeClMoO_4$, $CeClWO_4$, $CeBrMoO_4$, $CeBrWO_4$.
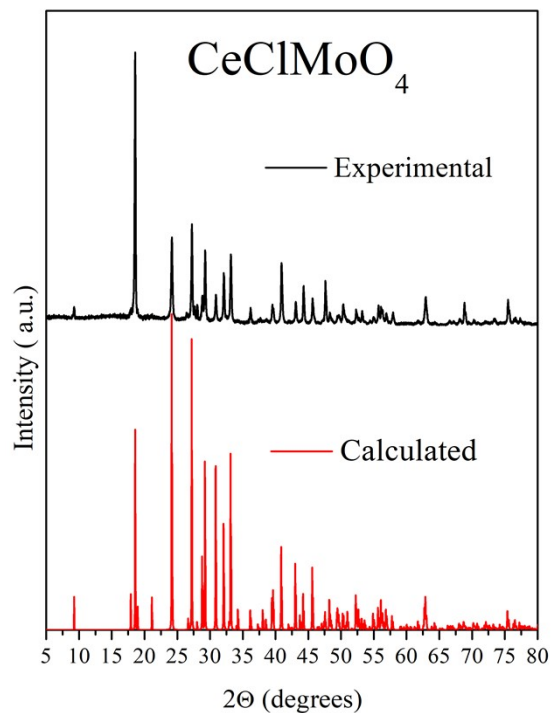
Figure S2. Experimental powder X-ray diffraction results of $CeClMoO_4$ with theoretical patterns shown at the bottom.
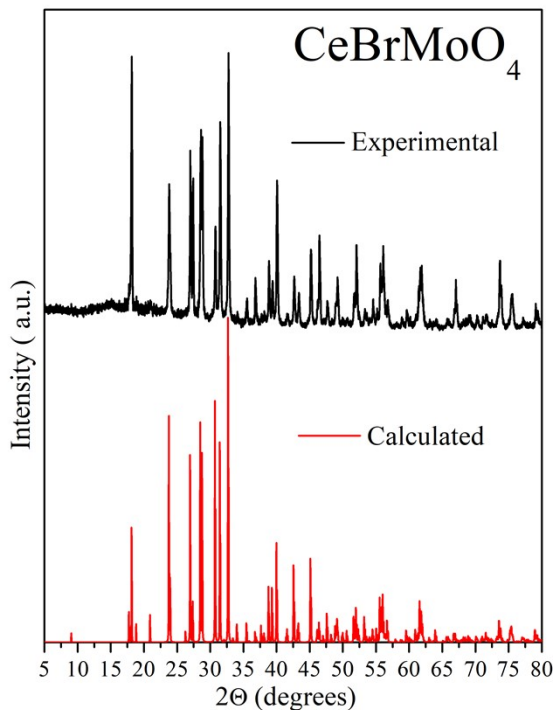
Figure S3. Experimental powder X-ray diffraction results of CeBrMoO$_4$ with theoretical patterns shown at the bottom.
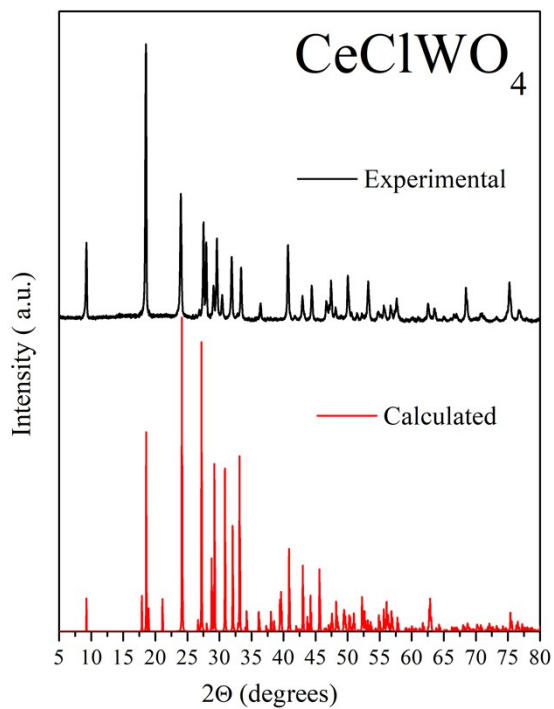
Figure S4. Experimental powder X-ray diffraction results of CeClWO$_4$ with theoretical patterns shown at the bottom.
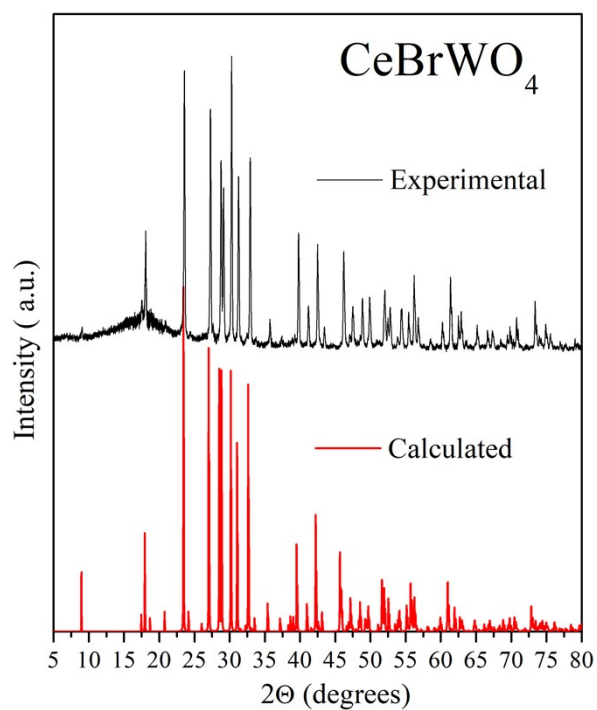
Figure S5. Experimental powder X-ray diffraction results of CeBrWO$_4$ with theoretical patterns shown at the bottom.
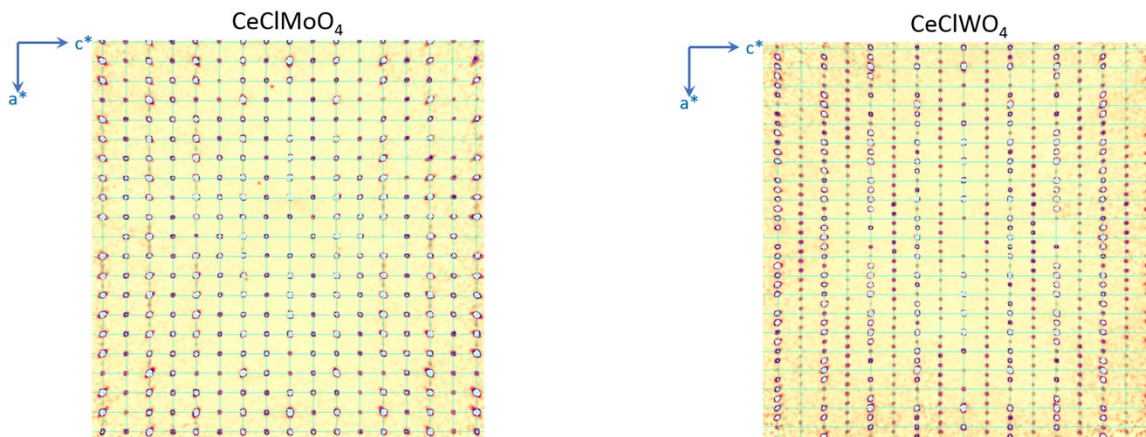
CeClMoO$_4$

CeClWO$_4$

Figure S6. The ($h1l$) planes of the reciprocal lattices of CeClMoO$_4$ and CeClWO$_4$.
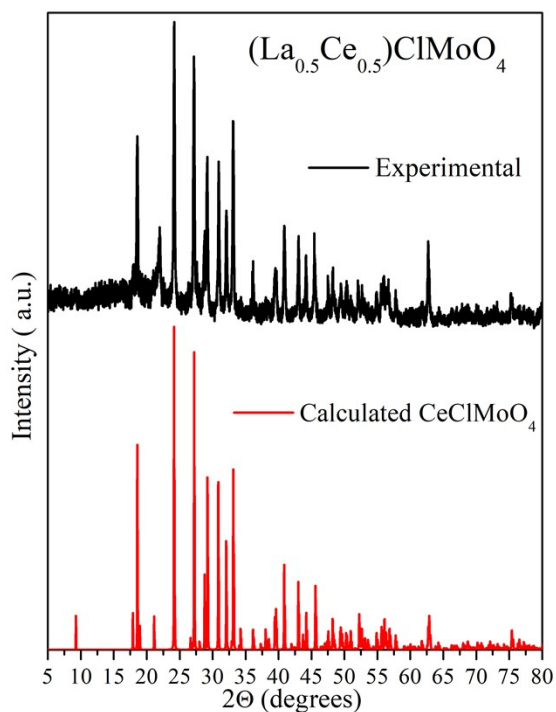
Figure S7. Experimental powder X-ray diffraction results of (La$_{0.5}$Ce$_{0.5}$)ClMoO$_4$ with theoretical patterns shown at the bottom.
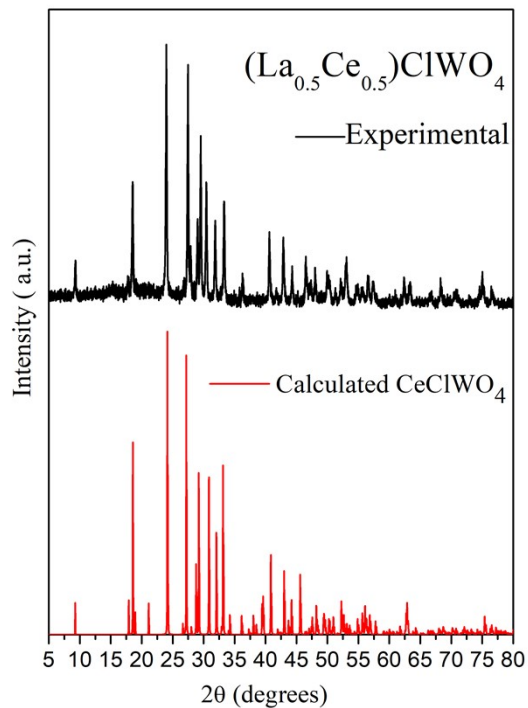
Figure S8. Experimental powder X-ray diffraction results of $(La_{0.5}Ce_{0.5})ClWO_4$ with theoretical patterns shown at the bottom.
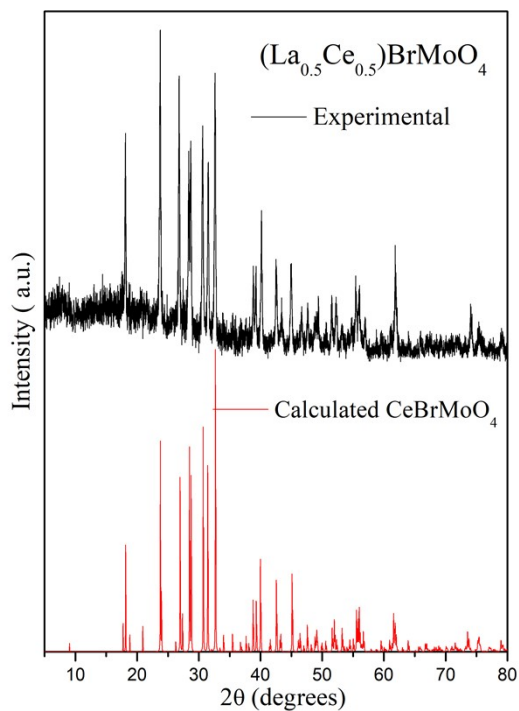
Figure S9. Experimental powder X-ray diffraction results of $(La_{0.5}Ce_{0.5})BrMoO_4$ with theoretical patterns shown at the bottom.
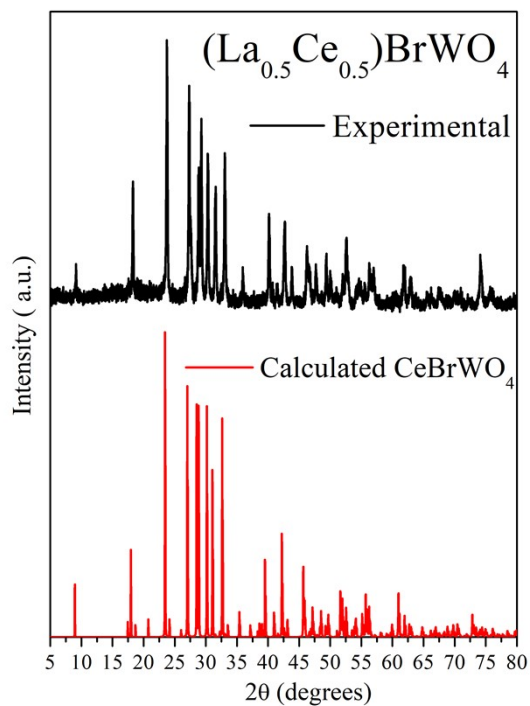
Figure S10. Experimental powder X-ray diffraction results of $(La_{0.5}Ce_{0.5})BrWO_4$ with theoretical patterns shown at the bottom.
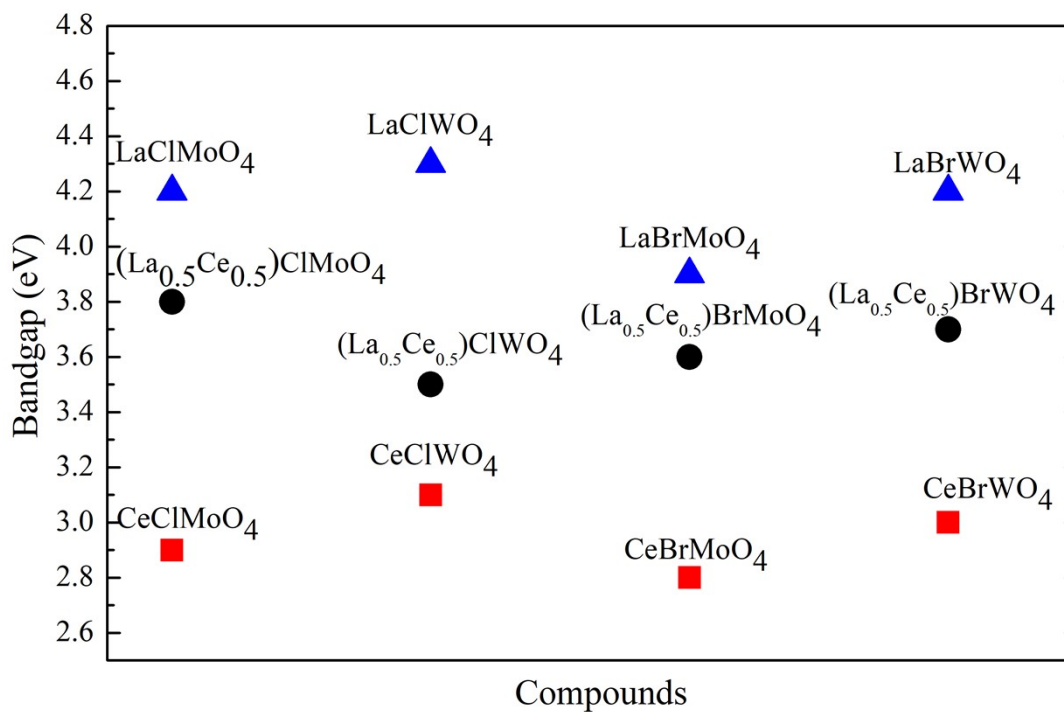
Figure S11. The comparison of bandgaps between $CeHaVIO_4$ (Ha=Cl, Br; VI=Mo, W), $LaHaVIO_4$ (Ha=Cl, Br; VI=Mo, W), and $(La_{0.5}Ce_{0.5})HaVIO_4$ (Ha=Cl, Br; VI=Mo, W).
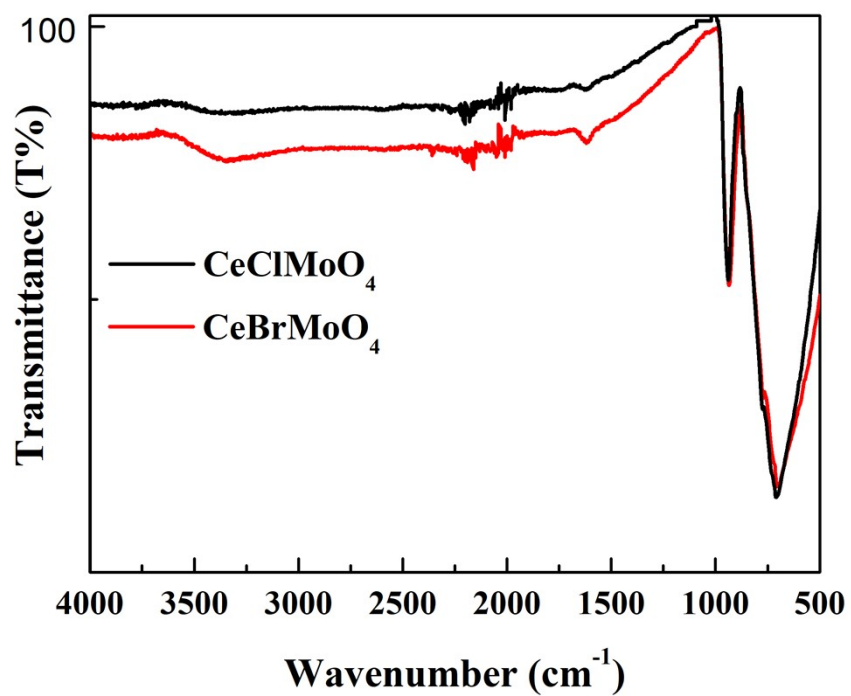
Figure S12. IR spectrum of CeClMoO$_4$ and CeBrMoO$_4$.
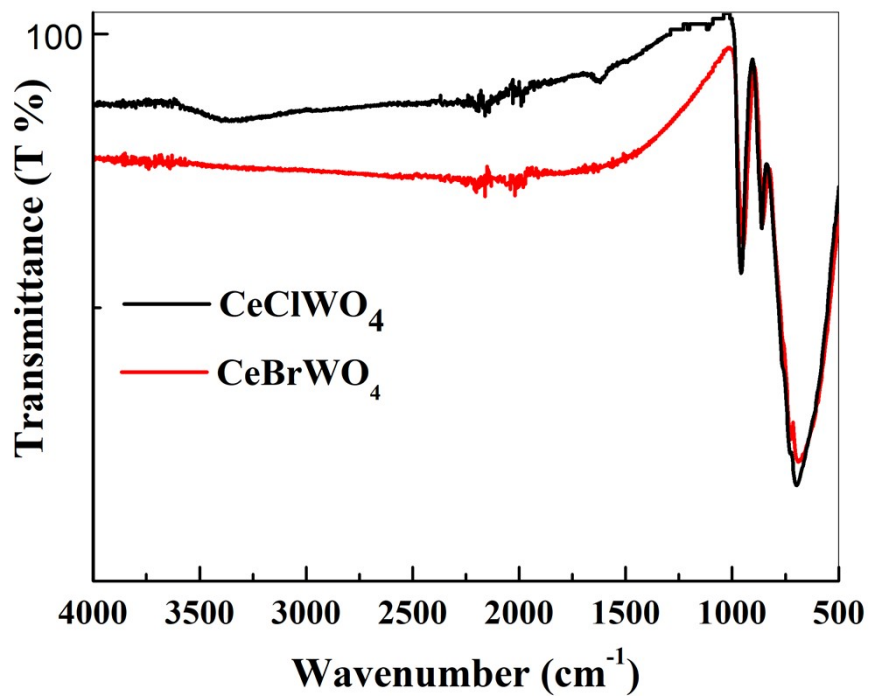
Figure S13. IR spectrum of CeClMoO$_4$ and CeBrMoO$_4$.
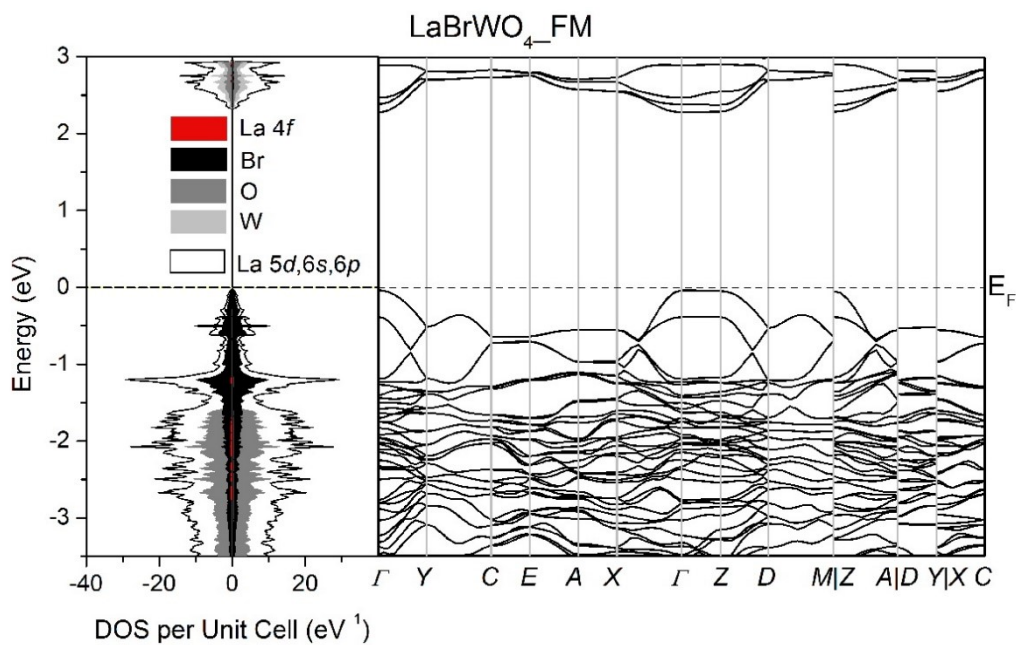
Figure S14. DOS and electronic band structure of $LaBrWO_4$ from antiferromagnetic calculation.
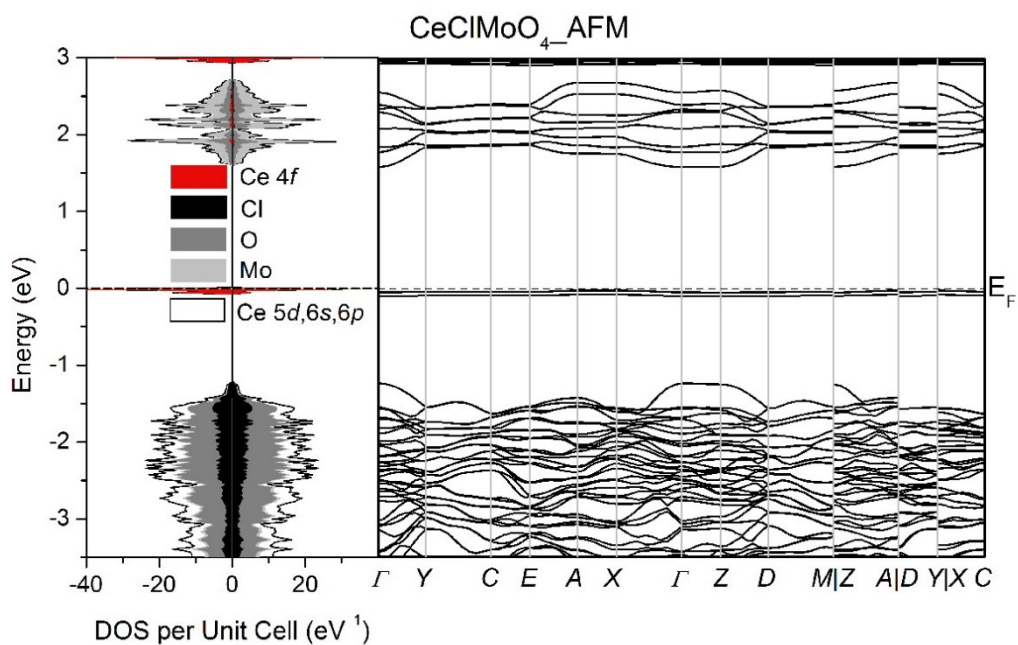
Figure S15. DOS and electronic band structure of $CeClMoO_4$ from antiferromagnetic calculation.
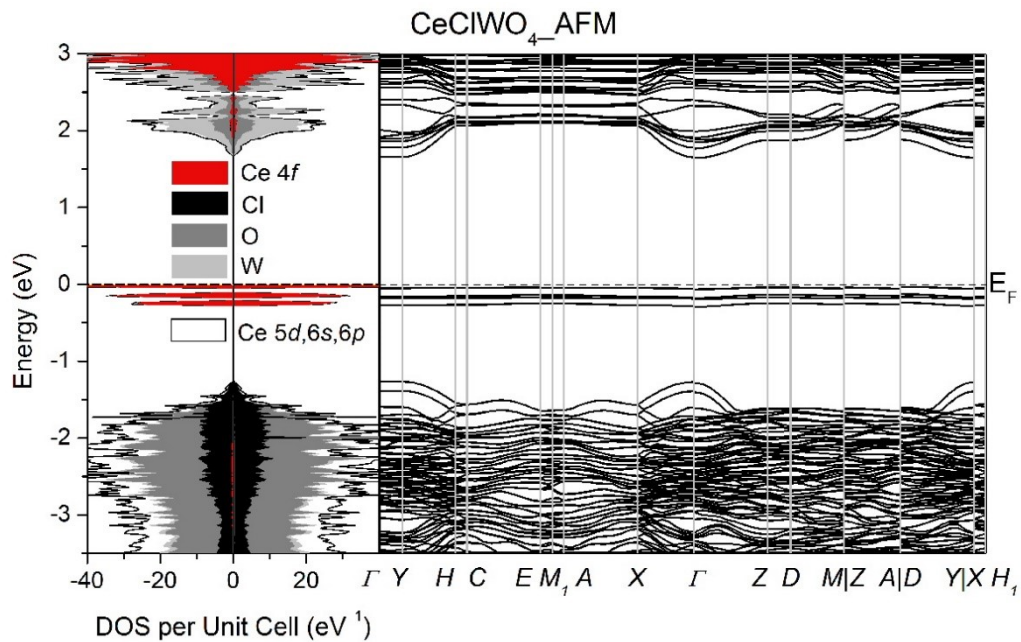
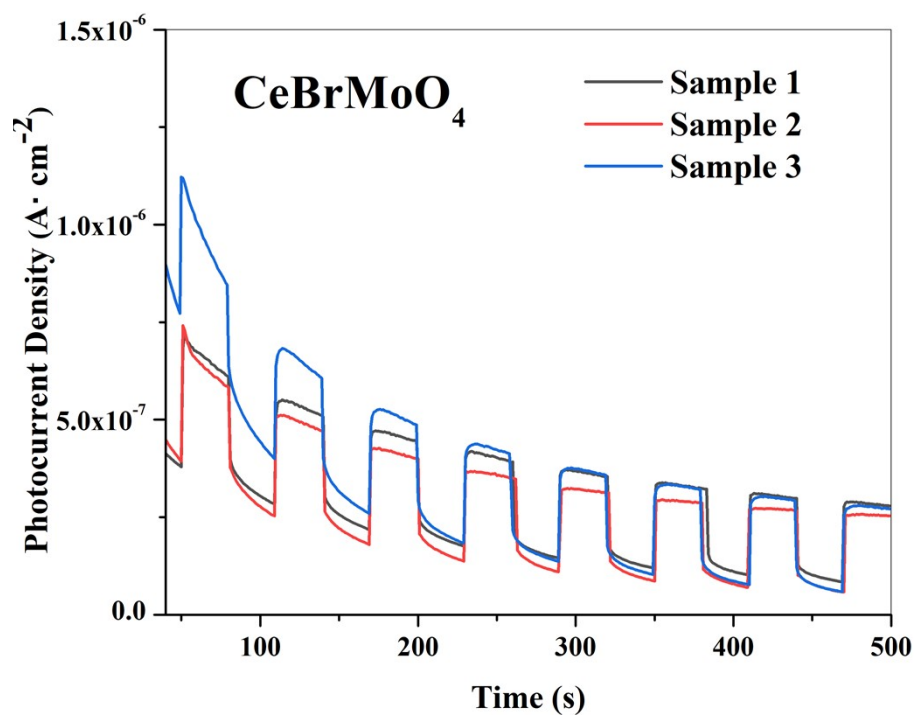**Figure S16.** DOS and electronic band structure of CeClWO$_4$ from antiferromagnetic calculation.
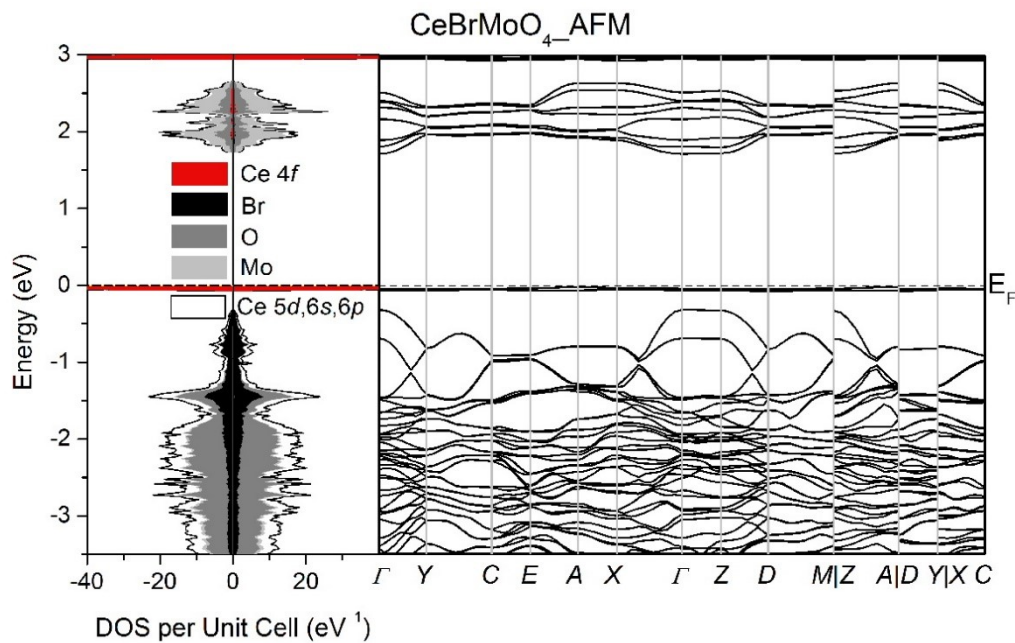
Figure S17. DOS and electronic band structure of CeBrMoO$_4$ from antiferromagnetic calculation.
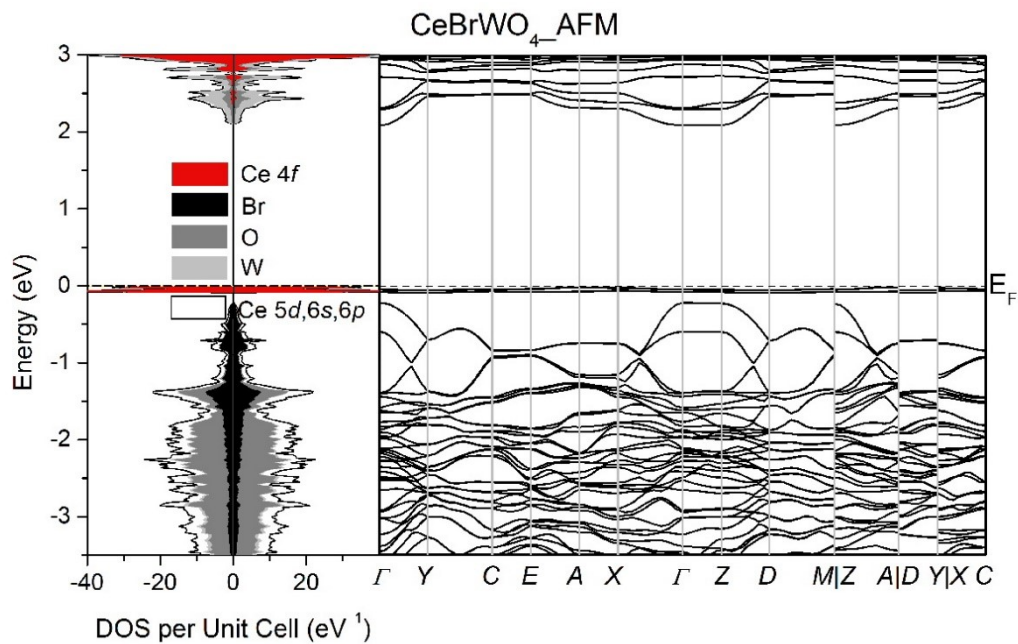
Figure S18. DOS and electronic band structure of CeBrWO$_4$ from antiferromagnetic calculation.

Figure S19. Photocurrent density of three samples of CeBrMoO$_4$.
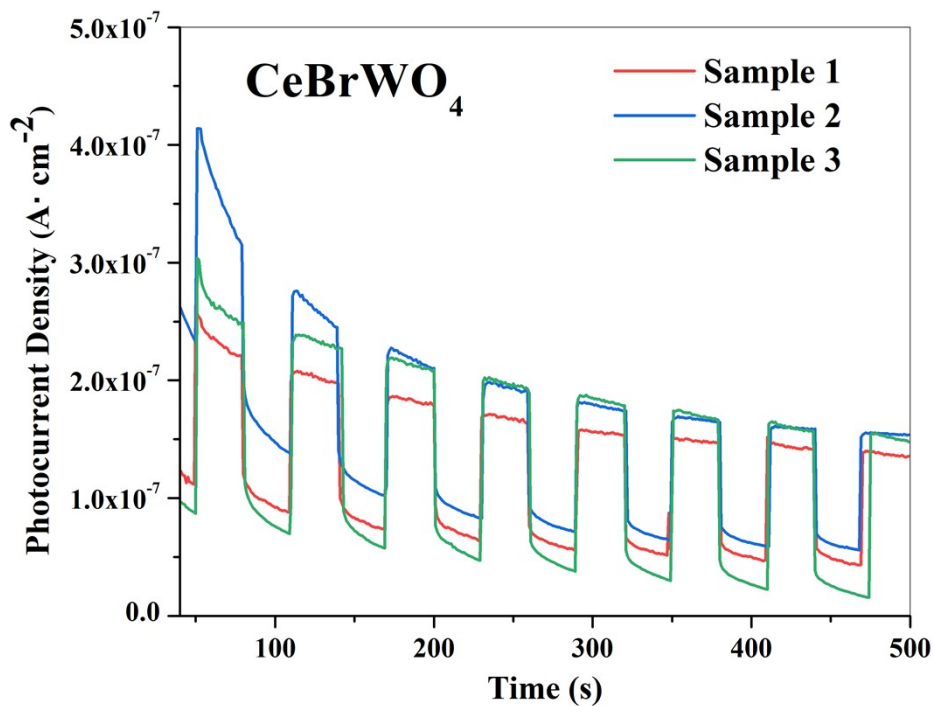
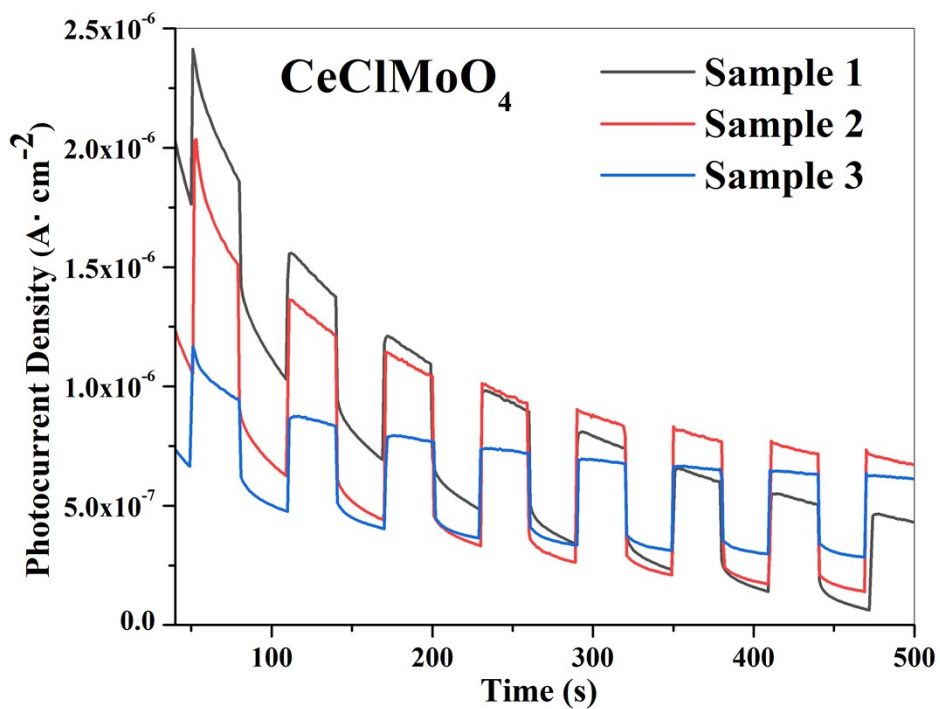**Figure S20.** Photocurrent density of three samples of CeBrWO$_4$.

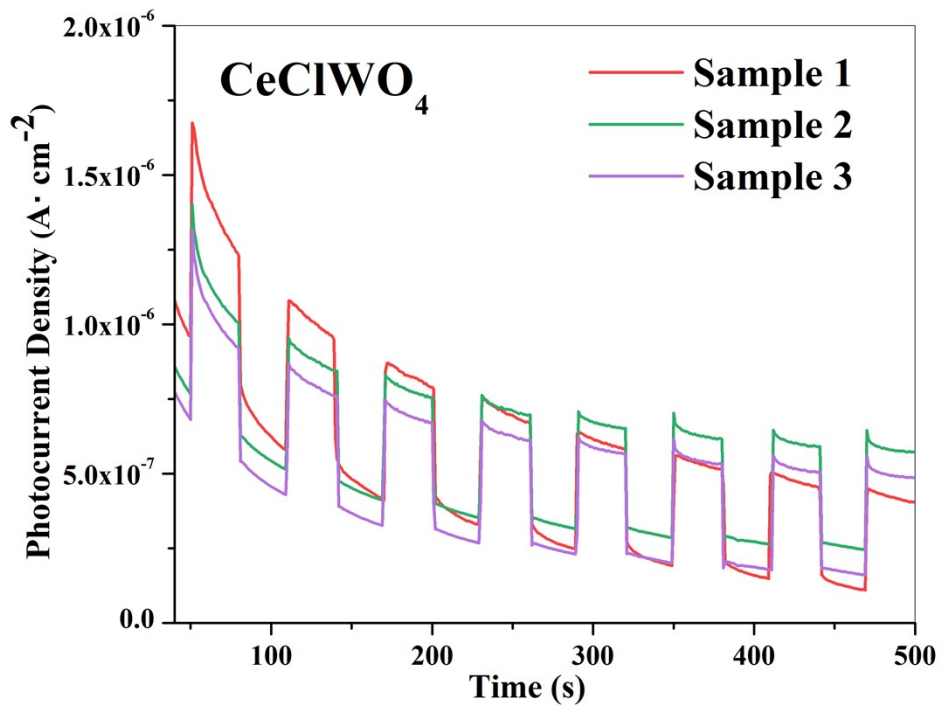**Figure S21.** Photocurrent density of three samples of CeClMoO$_4$.

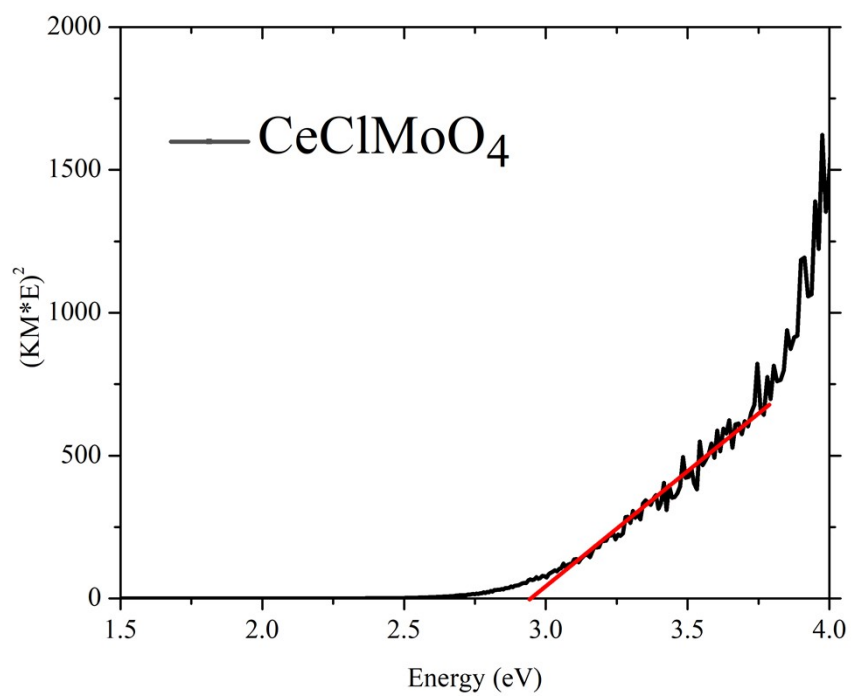**Figure S22.** Photocurrent density of three samples of CeClWO$_4$.

Figure S23. The allowed direct transitions of CeClMoO$_4$ sample.
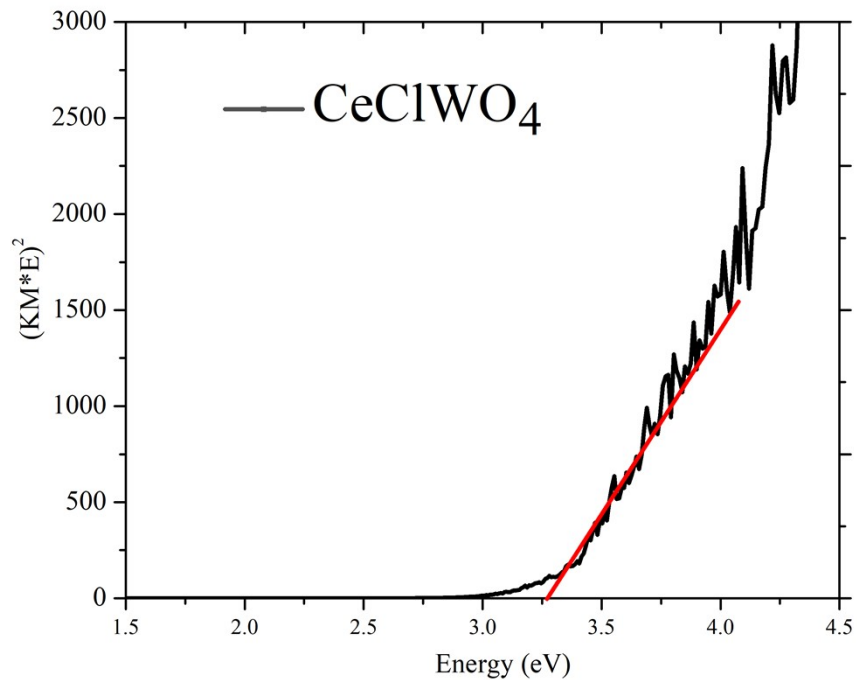
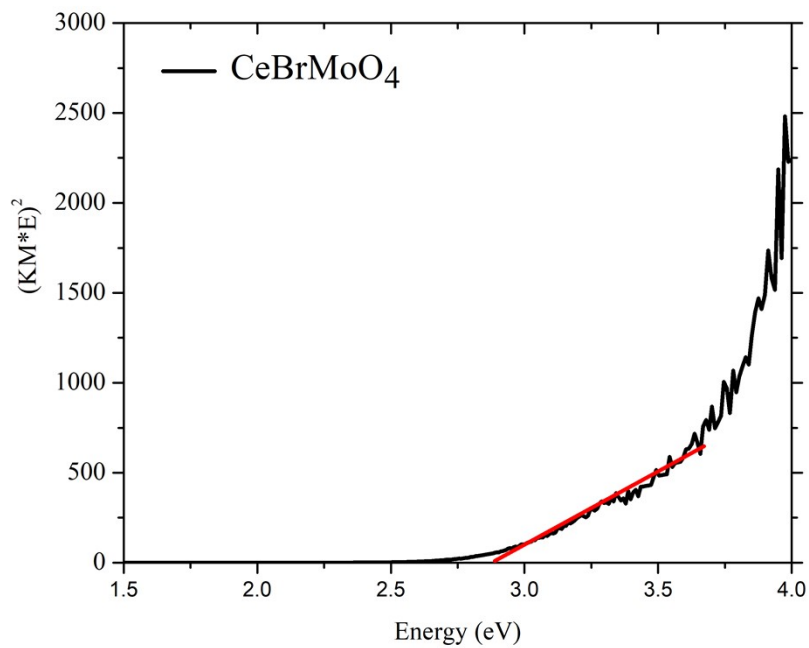**Figure S24.** The allowed direct transitions of CeClWO$_4$ sample.

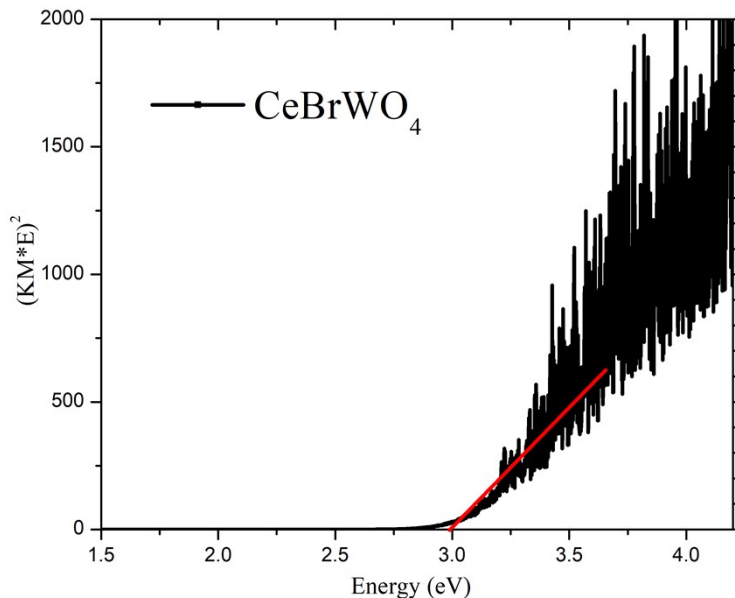**Figure S25.** The allowed direct transitions of CeBrMoO$_4$ sample.

Figure S26. The allowed direct transitions of two CeBrWO$_4$ sample.

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