Electronic Supplementary Information

Four Alkali Metal Molybdates with Two Types of Mo-O Chains, $ABMo_3O_{10}$ (A = Li, B = Rb; A = Li, Na, K, B = Cs): Synthesis, Structure Comparison and Optical Properties

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Table S1. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $LiRbMo_3O_{10}$ and $LiCsMo_3O_{10}$. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atoms	x	y	z	$U_{(eq)}$
		$LiRbMo_3O_{10}$		
Li(1)	514(17)	2500	1599(8)	36(3)
Rb(1)	3947(1)	-2500	4024(1)	26(1)
Mo(1)	1774(1)	2500	4047(1)	9(1)
Mo(2)	-1307(1)	-11(1)	3972(1)	9(1)
O(1)	1178(3)	119(3)	4367(2)	9(1)
O(2)	-807(5)	2500	4114(3)	10(1)
O(3)	-1299(5)	-2500	4325(3)	10(1)
O(4)	3759(5)	2500	4282(3)	16(1)
O(5)	1627(5)	2500	2800(3)	16(1)
O(6)	-3275(3)	401(4)	4040(2)	17(1)
O(7)	-932(3)	-299(4)	2760(2)	19(1)
		$LiCsMo_3O_{10}$		
Li(1)	541(12)	2500	1603(8)	29(3)
Cs(1)	6000(1)	2500	6014(1)	21(1)
Mo(1)	1744(1)	2500	4049(1)	9(1)
Mo(2)	1319(1)	-1(1)	5991(1)	9(1)
O(1)	1170(3)	127(3)	4386(2)	11(1)
O(2)	1355(4)	2500	5660(3)	13(1)
O(3)	796(4)	-2500	5837(3)	11(1)
O(4)	1536(4)	2500	2829(3)	16(1)
O(5)	3720(4)	2500	4224(3)	17(1)
O(6)	3270(3)	-444(4)	5964(2)	17(1)
O(7)	899(3)	258(4)	7172(2)	20(1)
		$NaCsMo_3O_{10}$		
Na(1)	574(4)	2500	2780(2)	21(1)
Cs(1)	1446(1)	2500	6489(1)	22(1)
Mo(1)	-2671(1)	2500	4434(1)	10(1)
Mo(2)	6095(1)	-12(1)	6006(1)	10(1)
O(1)	-3844(6)	2500	5743(3)	12(1)
O(2)	-3466(4)	138(4)	4642(2)	12(1)
O(3)	8189(4)	-329(5)	6299(2)	19(1)
O(4)	5038(5)	289(4)	6959(2)	20(1)
O(5)	5572(6)	-2500	5858(3)	13(1)
O(6)	-689(6)	2500	4883(3)	18(1)
O(7)	-2292(6)	2500	3334(3)	17(1)
		$KCsMo_3O_{10}$		
K(1)	-8456(3)	4782(3)	-2758(3)	22(1)

Cs(1)	-3100(1)	2695(1)	-864(1)	26(1)
Mo(1)	-337(1)	-685(1)	3555(1)	12(1)
Mo(2)	4497(1)	-1986(1)	5355(1)	13(1)
Mo(3)	2278(1)	1648(1)	1902(1)	13(1)
O(1)	4049(9)	1000(9)	3681(9)	12(1)
O(2)	257(9)	1541(9)	3993(9)	12(1)
O(3)	2627(9)	-1315(10)	3878(10)	15(2)
O(4)	464(10)	959(10)	1319(9)	16(2)
O(5)	4155(10)	-3751(10)	7303(10)	23(2)
O(6)	112(10)	-2756(11)	3350(10)	21(2)
O(7)	1625(10)	3989(11)	1169(11)	24(2)
O(8)	-2449(10)	266(11)	3093(10)	24(2)
O(9)	-3537(11)	-1430(12)	-259(11)	25(2)
O(10)	6007(10)	-3080(12)	4397(13)	30(2)

Table S2. Selected bond lengths (Å) and angles (deg.) for $LiRbMo_3O_{10}$.

Li(1)-O(5)	1.888(13)	Mo(1)-O(5)	1.699(4)
Li(1)-O(4)#12	1.916(14)	Mo(1)-O(4)	1.724(4)
Li(1)-O(6)#13	2.082(9)	Mo(1)-O(1)#1	1.918(3)
Li(1)-O(6)#3	2.082(9)	Mo(1)-O(1)	1.918(3)
Rb(1)-O(7)#5	2.940(3)	Mo(1)-O(2)	2.203(4)
Rb(1)-O(6)#2	3.123(4)	Mo(1)-O(3)#2	2.247(4)
Rb(1)-O(6)#8	3.123(4)	Mo(2)-O(7)	1.691(3)
Rb(1)-O(6)#9	3.228(4)	Mo(2)-O(6)	1.711(3)
Rb(1)-O(6)#10	3.228(4)	Mo(2)-O(3)	1.9400(19)
Rb(1)-O(7)#3	2.940(3)	Mo(2)-O(2)	1.9529(19)
Rb(1)-O(4)#6	3.021(5)	Mo(2)-O(1)	2.189(3)
Rb(1)-O(1)#7	3.116(3)	Mo(2)-O(1)#2	2.260(3)
Rb(1)-O(1)	3.116(3)		
O(4)-Mo(1)-O(1)	102.63(9)	O(7)#5-Rb(1)-O(1)	120.57(8)
O(1)#1-Mo(1)-O(1)	139.24(17)	O(7)#3-Rb(1)-O(1)	77.93(8)
O(5)-Mo(1)-O(2)	88.11(17)	O(7)#3-Rb(1)-O(6)#8	170.82(8)
O(4)-Mo(1)-O(2)	167.00(17)	O(1)#7-Rb(1)-O(1)	78.80(12)
O(1)#1-Mo(1)-O(2)	74.10(9)	O(7)#5-Rb(1)-O(6)#2	170.82(8)
O(6)-Mo(2)-O(1)	158.38(12)	O(5)-Li(1)-O(6)#13	96.4(5)
O(3)-Mo(2)-O(1)	88.83(13)	O(4)#12-Li(1)-O(6)#13	97.3(4)
O(2)-Mo(2)-O(1)	73.79(13)	O(5)-Li(1)-O(6)#3	96.4(5)
O(7)-Mo(2)-O(1)#2	163.31(12)	O(4)#12-Li(1)-O(6)#3	97.3(4)
O(6)-Mo(2)-O(1)#2	90.01(12)	O(6)#13-Li(1)-O(6)#3	99.2(6)

Symmetry transformations used to generate equivalent atoms:

#1 x, -y+1/2, z #2 -x, -y, -z+1 #3 x+1/2, y, -z+1/2 #4 x, y+1, z

#5 x+1/2, -y-1/2, -z+1/2 #6 -x+1, -y, -z+1 #7 x, -y-1/2, z #8 -x, y-1/2, -z+1

#9 x+1, y, z #10 x+1, -y-1/2, z #11 -x+1/2, -y, z+1/2 #12 x-1/2, y, -z+1/2

#13 x+1/2,-y+1/2,-z+1/2 #14 -x+1/2,-y,z-1/2 #15 x-1/2,y+1,-z+1/2 #16 x-1,y,z

Table S3. Selected bond lengths (Å) and angles (deg.) for $LiCsMo_3O_{10}$.

Li(1)-O(4)	1.909(11)	Mo(1)-O(4)	1.705(4)
Li(1)-O(5)#1	1.950(11)	Mo(1)-O(5)	1.727(4)
Li(1)-O(6)#2	2.066(8)	Mo(1)-O(1)	1.922(2)
Li(1)-O(6)#3	2.066(8)	Mo(1)-O(1)#9	1.922(2)
Cs(1)-O(7)#5	3.040(3)	Mo(1)-O(3)#11	2.203(4)
Cs(1)-O(7)#6	3.040(3)	Mo(1)-O(2)	2.264(4)
Cs(1)-O(5)	3.174(4)	Mo(2)-O(7)	1.693(3)
Cs(1)-O(1)#7	3.203(2)	Mo(2)-O(6)	1.721(3)
Cs(1)-O(1)#8	3.203(2)	Mo(2)-O(2)	1.9482(11)
Cs(1)-O(6)#8	3.220(3)	Mo(2)-O(3)	1.9567(11)
Cs(1)-O(6)#7	3.220(3)	Mo(2)-O(1)#11	2.218(3)
Cs(1)-O(6)	3.248(3)	Mo(2)-O(1)	2.235(3)
Cs(1)-O(6)#9	3.248(3)		
O(4)-Li(1)-O(5)#1	152.9(6)	O(5)-Mo(1)-O(1)	102.80(8)
O(4)-Li(1)-O(6)#2	99.1(4)	O(4)-Mo(1)-O(1)#9	102.45(9)
O(5)#1-Li(1)-O(6)#2	98.6(4)	O(4)-Mo(1)-O(3)#11	88.09(16)
O(4)-Li(1)-O(6)#3	99.1(4)	O(1)-Mo(1)-O(2)	73.75(8)
O(5)#1-Li(1)-O(6)#3	98.6(4)	O(3)#11-Mo(1)-O(2)	77.33(14)
O(6)#2-Li(1)-O(6)#3	97.7(5)	O(7)-Mo(2)-O(6)	104.73(13)
O(7)#5-Cs(1)-O(7)#6	67.86(11)	O(7)-Mo(2)-O(2)	96.89(14)
O(7)#6-Cs(1)-O(5)	129.17(7)	O(2)-Mo(2)-O(3)	156.52(16)
O(7)#5-Cs(1)-O(1)#7	79.60(7)	O(7)-Mo(2)-O(1)#11	91.49(12)
O(7)#5-Cs(1)-O(1)#8	120.83(7)	O(6)-Mo(2)-O(1)#11	159.77(11)

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2, y, -z+1/2 #2 -x+1/2, y+1/2, z-1/2 #3 -x+1/2, -y, z-1/2

#4 -x+1/2, -y+1, z-1/2 #5 x+1/2, -y+1/2, -z+3/2 #6 x+1/2, y, -z+3/2

#7 -x+1, y+1/2, -z+1 #8 -x+1, -y, -z+1 #9 x, -y+1/2, z

#10 x+1/2, y, -z+1/2 #11 -x, -y, -z+1 #12 -x+1, -y+1, -z+1

#13 x, -y-1/2, z #14 -x+1/2, -y, z+1/2 #15 x-1/2, y, -z+3/2

Table S4. Selected bond lengths (Å) and angles (deg.) for $NaCsMo_3O_{10}$.

Na(1)-O(7)	2.384(5)	Cs(1)-O(4)#12	3.334(4)
Na(1)-O(3)#1	2.390(4)	Mo(1)-O(6)	1.688(5)
Na(1)-O(3)#2	2.390(4)	Mo(1)-O(7)	1.739(5)
Na(1)-O(7)#3	2.399(6)	Mo(1)-O(2)#12	1.928(3)
Na(1)-O(4)#4	2.524(4)	Mo(1)-O(2)	1.928(3)
Na(1)-O(4)#5	2.524(4)	Mo(1)-O(1)	2.237(5)
Cs(1)-O(6)	3.004(5)	Mo(1)-O(5)#6	2.294(5)
Cs(1)-O(2)#6	3.097(3)	Mo(2)-O(3)	1.703(3)
Cs(1)-O(2)#7	3.097(3)	Mo(2)-O(4)	1.712(4)
Cs(1)-O(4)#8	3.144(4)	Mo(2)-O(5)	1.9503(16)
Cs(1)-O(4)#9	3.144(4)	Mo(2)-O(1)#15	1.9562(15)
Cs(1)-O(3)#10	3.331(4)	Mo(2)-O(2)#15	2.158(3)
Cs(1)-O(3)#11	3.331(4)	Mo(2)-O(2)#6	2.276(3)
Cs(1)-O(4)	3.334(4)		
O(4)#8-Cs(1)-O(3)#10	98.72(10)	O(6)-Mo(1)-O(7)	104.8(2)
O(7)-Na(1)-O(3)#2	98.94(15)	O(6)-Mo(1)-O(2)#12	102.75(11)
O(3)#1-Na(1)-O(3)#2	87.5(2)	O(2)#12-Mo(1)-O(2)	137.65(18)
O(7)-Na(1)-O(7)#3	154.86(18)	O(6)-Mo(1)-O(1)	89.5(2)
O(2)#6-Cs(1)-O(4)#8	163.95(9)	O(7)-Mo(1)-O(1)	165.7(2)
O(2)#7-Cs(1)-O(4)#8	105.49(9)	O(2)#12-Mo(1)-O(1)	73.51(10)
O(6)-Cs(1)-O(4)#9	116.83(10)	O(3)-Mo(2)-O(4)	103.96(17)
O(2)#7-Cs(1)-O(3)#10	138.70(9)	O(3)-Mo(2)-O(5)	95.30(17)
O(4)#8-Cs(1)-O(4)#9	64.73(13)	O(4)-Mo(2)-O(5)	97.66(18)
O(6)-Cs(1)-O(3)#10	60.55(9)	O(3)-Mo(2)-O(1)#15	99.90(18)
O(2)#6-Cs(1)-O(3)#10	85.02(9)	O(4)-Mo(2)-O(1)#15	93.57(17)
O(6)-Cs(1)-O(4)	130.04(9)	O(5)-Mo(2)-O(1)#15	158.33(19)
O(2)#6-Cs(1)-O(4)	51.40(9)	O(3)-Mo(2)-O(2)#15	97.02(15)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, y+1/2, -z+1 #2 -x+1, -y, -z+1 #3 x+1/2, y, -z+1/2 #4 -x+1/2, -y, z-1/2

#5 -x+1/2, y+1/2, z-1/2 #6 -x, -y, -z+1 #7 -x, y+1/2, -z+1 #8 x-1/2, -y+1/2, -z+3/2

#9 x-1/2, y, -z+3/2 #10 x-1, y, z #11 x-1, -y+1/2, #12 x, y+1/2, z

#13 x-1/2, y, -z+1/2 #14 -x, -y+1, -z+1 #15 x+1, y, z #16 -x+1/2, -y, z+1/2

#17 x+1/2, y ,-z+3/2 #18 x, -y-1/2, z

Table S5. Selected bond lengths (Å) and angles (deg.) for $KCsMo_3O_{10}$.

K(1)-O(6)#1	2.629(8)	Mo(1)-O(8)	1.691(9)
K(1)-O(2)#2	2.731(8)	Mo(1)-O(6)	1.725(8)
K(1)-O(5)#3	2.739(9)	Mo(1)-O(2)#7	1.852(7)
K(1)-O(10)#4	2.762(9)	Mo(1)-O(4)	1.957(7)
K(1)-O(9)#1	2.948(9)	Mo(1)-O(2)	2.195(7)
K(1)-O(7)#2	2.964(9)	Mo(1)-O(3)	2.353(8)
K(1)-O(7)#5	3.056(10)	Mo(2)-O(10)	1.694(8)
K(1)-O(6)#3	3.090(9)	Mo(2)-O(5)	1.706(7)
Cs(1)-O(5)#3	2.995(8)	Mo(2)-O(3)	1.843(8)
Cs(1)-O(8)	3.016(9)	Mo(2)-O(1)#9	1.992(7)
Cs(1)-O(6)#4	3.089(8)	Mo(2)-O(1)	2.166(7)
Cs(1)-O(9)#1	3.142(9)	Mo(3)-O(7)	1.680(8)
Cs(1)-O(3)#4	3.150(8)	Mo(3)-O(9)#4	1.700(8)
Cs(1)-O(7)#6	3.176(9)	Mo(3)-O(4)	1.891(8)
Cs(1)-O(4)	3.184(8)	Mo(3)-O(1)	1.950(7)
Cs(1)-O(9)	3.319(10)	Mo(3)-O(3)	2.214(8)
Cs(1)-O(4)#4	3.349(8)	Mo(3)-O(2)	2.307(7)
Cs(1)-O(5)#7	3.443(9)		
O(6)#1-K(1)-O(2)#2	112.2(3)	O(6)-Mo(1)-O(2)#7	101.8(3)
O(6)#1-K(1)-O(5)#3	159.1(3)	O(8)-Mo(1)-O(4)	98.7(4)
O(6)#1-K(1)-O(10)#4	79.9(3)	O(2)#7-Mo(1)-O(4)	144.7(3)
O(6)#1-K(1)-O(9)#1	91.1(3)	O(6)-Mo(1)-O(2)	155.7(3)
O(6)#1-K(1)-O(7)#2	84.5(3)	O(2)#7-Mo(1)-O(2)	75.1(3)
O(7)#2-K(1)-O(7)#5	60.5(3)	O(2)#7-Mo(1)-O(3)	84.4(3)
O(6)#1-K(1)-O(6)#3	76.3(3)	O(4)-Mo(1)-O(3)	71.7(3)
O(5)#3-Cs(1)-O(6)#4	108.3(2)	O(5)-Mo(2)-O(3)	104.7(4)
O(8)-Cs(1)-O(6)#4	119.4(2)	O(10)-Mo(2)-O(1)#9	98.9(4)
O(5)#3-Cs(1)-O(9)#1	76.2(2)	O(1)#9-Mo(2)-O(1)	71.6(3)
O(9)#1-Cs(1)-O(3)#4	91.7(2)	O(4)-Mo(3)-O(2)	71.3(3)
O(5)#3-Cs(1)-O(7)#6	73.6(2)	O(1)-Mo(3)-O(2)	90.2(3)
O(7)#6-Cs(1)-O(4)	70.9(2)	O(3)-Mo(3)-O(2)	71.6(3)
O(5)#3-Cs(1)-O(9)	121.6(2)	O(7)-Mo(3)-Mo(1)	118.7(3)
O(8)-Cs(1)-O(9)	75.4(2)		

Symmetry transformations used to generate equivalent atoms:

#1 -x-1, -y, -z #2 -x-1, -y+1, -z #3 x-1, y+1, z-1 #4 -x, -y, -z

#5 x-1, y, z #6 -x, -y+1, -z #7 -x, -y, -z+1 #8 x+1, y-1, z+1

#9 -x+1, -y, -z+1 #10 x+1, y, z

Figure S1 (a) The arrangement of LiO_4 in $LiCsMo_3O_{10}$; (b) The arrangement of the CsO_9 polyhedra in $LiCsMo_3O_{10}$.

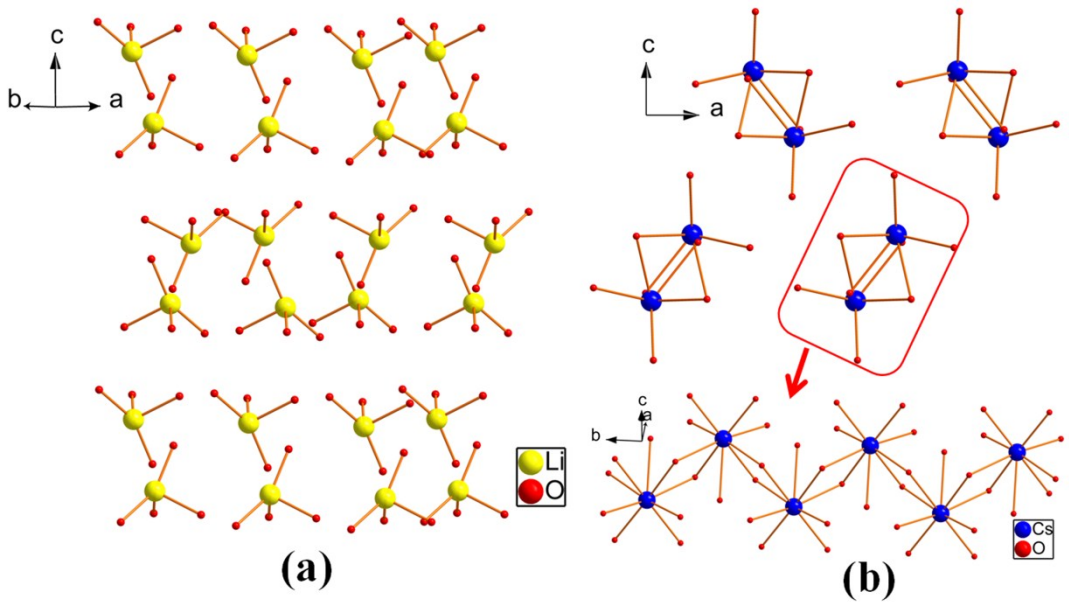

Figure S2 (a) The arrangement of NaO_6 in $NaCsMo_3O_{10}$; (b) The arrangement of the CsO_9 polyhedra in $NaCsMo_3O_{10}$.

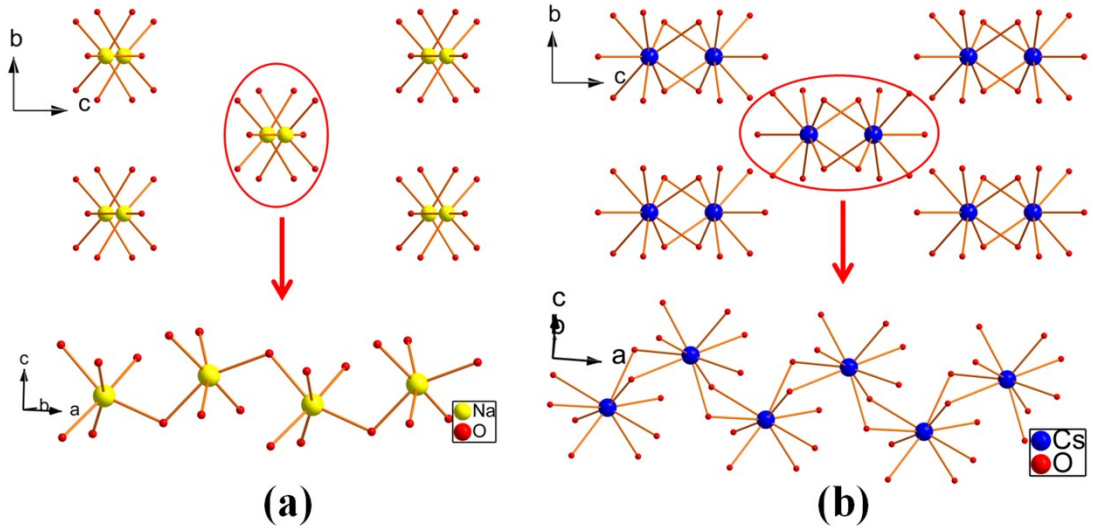

Figure S3 (a) The arrangement of KO_8 in $KCsMo_3O_{10}$; (b) The arrangement of CsO_{10} the polyhedra in $KCsMo_3O_{10}$.

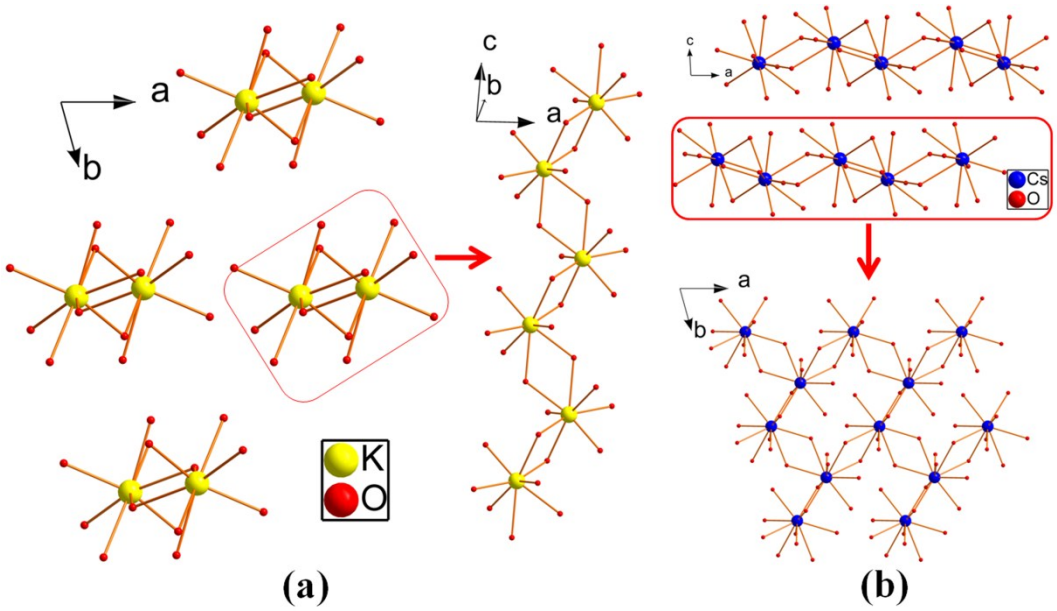

Figure S4 (a) The Mo-O chain in $LiCsMo_3O_{10}$; (b) The Mo-O chain in $NaCsMo_3O_{10}$; (c) The Mo-O chain in $KCsMo_3O_{10}$.

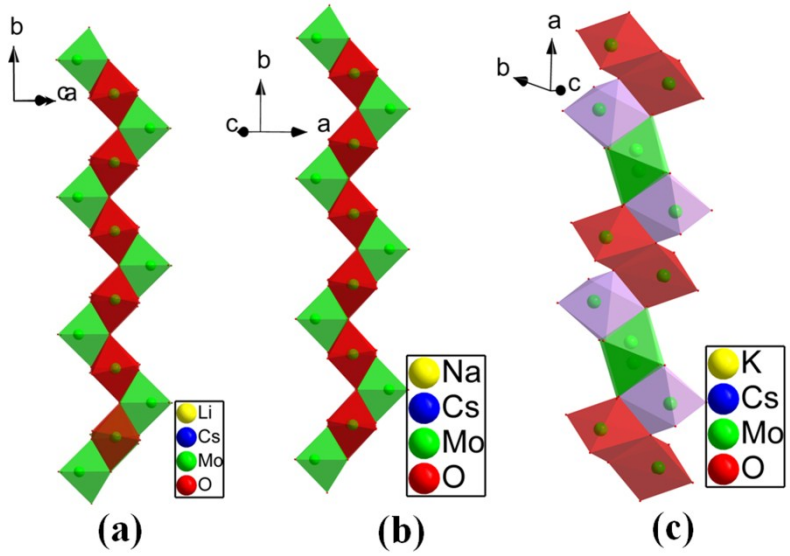

Figure S5 The infrared spectra of $LiRbMo_3O_{10}$, $LiCsMo_3O_{10}$, $NaCsMo_3O_{10}$ and $KCsMo_3O_{10}$.

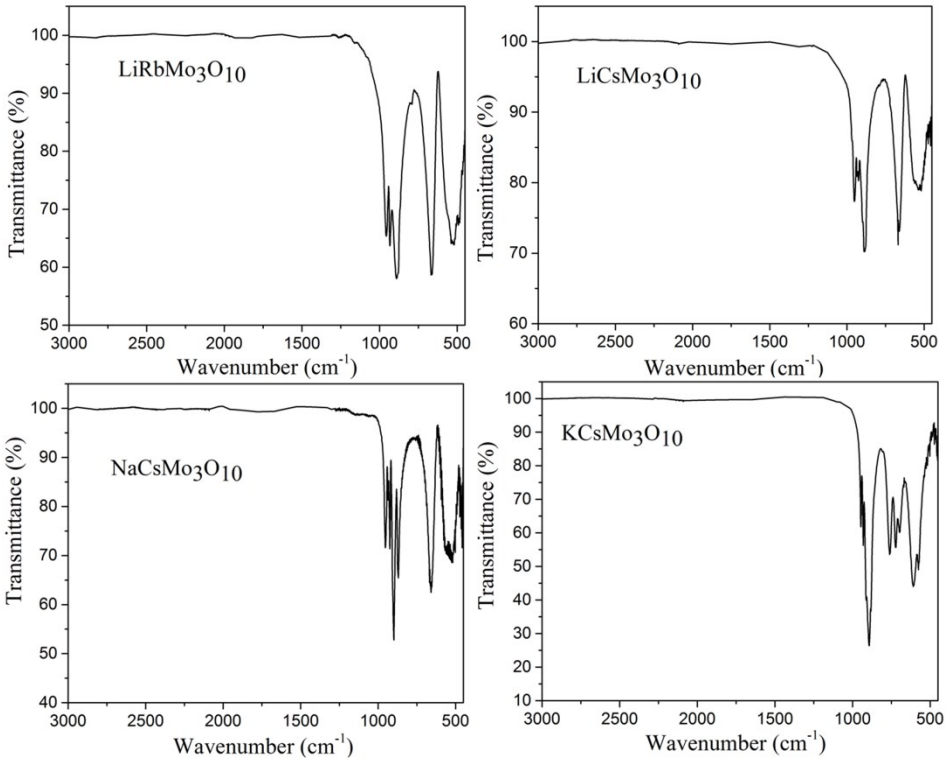

Figure S6 The band structure (left) and projected density of states (PDOS) (right) of $LiRbMo_3O_{10}$.

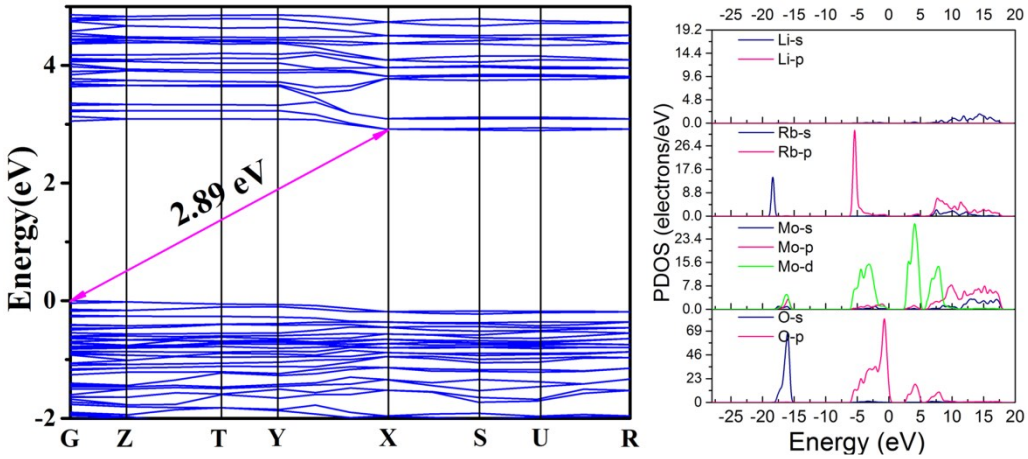

Figure S7 The band structure (left) and projected density of states (PDOS) (right) of $LiCsMo_3O_{10}$.

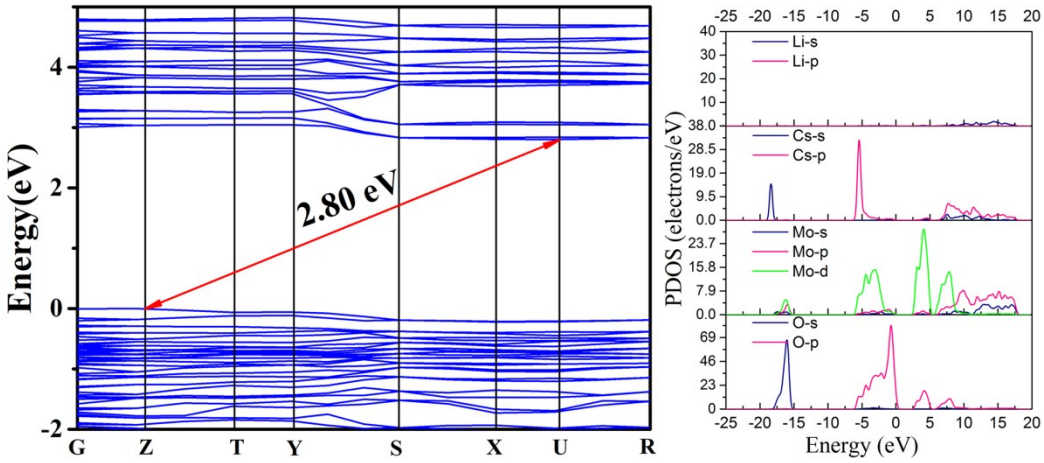

Figure S8 The band structure (left) and projected density of states (PDOS) (right) of $NaCsMo_3O_{10}$.

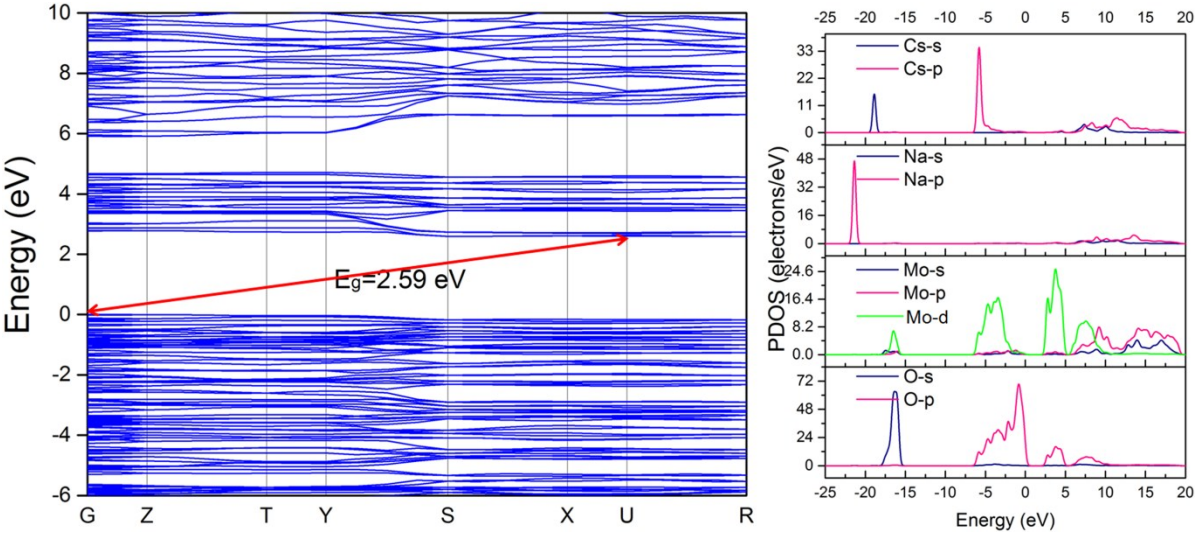

Figure S9 The band structure (left) and projected density of states (PDOS) (right) of $KCsMo_3O_{10}$.