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Supporting Information

$LiMCO_3$ (M=K,Rb,Cs): a series of mixed alkali carbonates with large birefringence

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TableS1. Atomic coordinates and equivalent isotropic displacement parameters of $LiRbCO_3$ and $LiCsCO_3$.

Atom	Wyck	x/a	y/b	z/c	U[Å2]	BVS
			$LiRbCO_3$			
Li1	4e	0.6033(8)	0.4284(8)	0.1956(7)	0.0176(10)	1.05
Rb1	4e	0.16389(4)	0.35911(4)	0.33314(4)	0.01744(12)	1.17
C1	4e	0.2158(5)	0.3321(4)	-0.0905(4)	0.0132(6)	3.95
O1	4e	0.2971(3)	0.4721(3)	0.0261(3)	0.0158(4)	2.07
O2	4e	0.1285(3)	0.1934(3)	-0.0462(3)	0.0190(4)	2.03
O3	4e	0.2264(4)	0.3336(3)	-0.2586(3)	0.0196(5)	2.06
			$LiCsCO_3$			
Li1	4e	0.1021(8)	0.4247(8)	1.1857(7)	0.0207(10)	1.02
Cs1	4e	0.16088(3)	0.13362(2)	0.82465(2)	0.02042(9)	1.04
C1	4e	-0.2208(5)	-0.1676(4)	0.5999(4)	0.0151(5)	4.01
O1	4e	0.1928(3)	0.5352(3)	0.9812(3)	0.0203(4)	2.04
O2	4e	0.2350(4)	0.1652(3)	1.2424(3)	0.0226(5)	2.01
O3	4e	0.3783(4)	-0.2018(3)	1.0676(3)	0.0240(5)	2.01

TableS2. Selected bond distances (Å) and angles (deg.) for $LiRbCO_3$.

$LiRbCO_3$			
Rb1-O2$^{\#1}$	2.899(2)	O1-Li1-O1$^{\#7}$	92.6(2)
Rb1-O3$^{\#2}$	2.923(2)	O3$^{\#7}$-Li1-O1$^{\#7}$	64.08(16)
Rb1-O1	2.932(2)	O3$^{\#4}$-Li1-O1$^{\#7}$	101.1(2)
Rb1-O1$^{\#3}$	2.940(2)	O2$^{\#4}$-Li1-O1$^{\#7}$	158.6(3)
Rb1-O2$^{\#4}$	2.942(2)	O2$^{\#1}$-Rb1-O3$^{\#2}$	69.54(6)
Rb1-O2	3.005(2)	O2$^{\#1}$-Rb1-O1	87.98(6)
Rb1-O3$^{\#5}$	3.101(3)	O3$^{\#2}$-Rb1-O1	152.74(6)
Rb1-O3$^{\#6}$	3.322(2)	O2$^{\#1}$-Rb1-O1$^{\#3}$	129.14(6)
Rb1-O1$^{\#6}$	3.396(2)	O3$^{\#2}$-Rb1-O1$^{\#3}$	67.15(6)
C1-O1	1.292(3)	O1-Rb1-O1$^{\#3}$	122.17(5)
C1-O2	1.274(3)	O2$^{\#1}$-Rb1-O2$^{\#4}$	73.79(7)
C1- O3	1.298(3)	O3$^{\#2}$-Rb1-O2$^{\#4}$	90.46(6)
Li1-O1	1.967(5)	O1-Rb1-O2$^{\#4}$	67.86(6)
Li1$^{\#7}$-O1	2.172(5)	O1$^{\#3}$-Rb1-O2$^{\#4}$	81.13(6)
Li1$^{\#8}$-O2	2.070(5)	O2$^{\#1}$-Rb1-O2	132.50(5)
Li1$^{\#7}$-O3	2.006(6)	O3$^{\#2}$-Rb1-O2	152.99(6)
Li1$^{\#8}$-O3	2.026(6)	O1-Rb1-O2	44.59(6)
O2-C1-O1	122.8(3)	O1$^{\#3}$-Rb1-O2	85.89(6)
O2-C1-O3	119.1(3)	O2$^{\#1}$-Rb1-O3$^{\#5}$	133.88(6)
O1-C1-O3	118.1(3)	O2$^{\#4}$-Rb1-O2	83.44(5)
O1-Li1-O3$^{\#7}$	111.9(3)	O3$^{\#2}$-Rb1-O3$^{\#5}$	84.56(5)
O1-Li1-O3$^{\#4}$	120.7(3)	O1-Rb1-O3$^{\#5}$	122.68(6)
O3$^{\#7}$-Li1-O3$^{\#4}$	126.1(2)	O1$^{\#3}$-Rb1-O3$^{\#5}$	65.98(6)
O1-Li1-O2$^{\#4}$	108.6(2)	O2$^{\#4}$-Rb1-O3$^{\#5}$	146.06(6)
O3$^{\#7}$-Li1-O2$^{\#4}$	109.1(3)	O2-Rb1-O3$^{\#5}$	85.98(5)
O3$^{\#4}$-Li1-O2$^{\#4}$	65.54(18)		

Symmetry transformations used to generate equivalent atoms:

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

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

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

TableS3. Selected bond distances (Å) and angles (deg.) for $LiCsCO_3$.

$LiCsCO_3$			
Cs1-O1	3.102(4)	O2-Li1-O3$^{\#2}$	64.55(19)
Cs1-O2	3.097(4)	O1$^{\#1}$-Li1-O1	92.7(2)
Cs1-O3	3.048(3)	O2$^{\#2}$-Li1-O1	63.92(18)
Cs1-O1$^{\#4}$	3.107(3)	O2-Li1-O1	103.2(2)
Cs1-O3$^{\#5}$	3.108(4)	O3$^{\#2}$-Li1-O1	160.2(3)
Cs1-O3$^{\#6}$	3.198(4)	O3$^{\#8}$-C1-O1$^{\#7}$	122.5(3)
Cs1-O2$^{\#7}$	3.209(4)	O3$^{\#8}$-C1-O2$^{\#3}$	119.5(3)

Cs1-O1$^{\#4}$	3.107(3)	O1$^{\#7}$-C1-O2$^{\#3}$	118.0(3)
Cs1-O1$^{\#5}$	3.108(4)	O3-Cs1-O2$^{\#3}$	76.82(9)
Cs1-O1$^{\#6}$	3.198(4)	O1-Cs1-O2$^{\#3}$	87.33(6)
Cs1-O1$^{\#7}$	3.209(4)	O1-Cs1-O2$^{\#3}$	123.53(7)
Li1-O1$^{\#1}$	1.981(6)	O1$^{\#4}$-Cs1-O2$^{\#3}$	106.62(7)
Li1-O1$^{\#2}$	2.027(6)	O1$^{\#5}$-Cs1-O1$^{\#3}$	150.21(7)
Li1-O1	2.054(6)	O1$^{\#6}$-Cs1-O1$^{\#3}$	111.56(6)
Li1-O1$^{\#2}$	2.090(6)	O1$^{\#7}$-Cs1-O1$^{\#3}$	65.35(8)
Li1-O1	2.139(6)	C1-Cs1-O1$^{\#3}$	21.88(7)
C1-O1$^{\#8}$	1.272(4)	O1-Cs1-O1$^{\#7}$	105.75(8)
C1-O1$^{\#7}$	1.286(4)	O1-Cs1-O1$^{\#7}$	120.18(8)
C1-O1$^{\#3}$	1.289(4)	O1-Cs1-O1$^{\#7}$	120.39(7)
O1$^{\#1}$-Li1-O1$^{\#2}$	113.0(3)	O1$^{\#4}$-Cs1-O1$^{\#7}$	82.49(10)
O1$^{\#1}$-Li1-O1	122.9(3)	O1$^{\#5}$-Cs1-O1$^{\#7}$	146.00(6)
O1$^{\#2}$-Li1-O1	123.4(3)	O1$^{\#6}$-Cs1-O1$^{\#7}$	74.77(8)
O1$^{\#1}$-Li1-O1$^{\#2}$	107.1(3)	O1$^{\#7}$-Cs1-O1$^{\#7}$	58.47(8)
O1$^{\#2}$-Li1-O1$^{\#2}$	108.4(3)	O1$^{\#3}$-Cs1-O1$^{\#7}$	37.09(6)

Symmetry transformations used to generate equivalent atoms:

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

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

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

TableS4. The bond-length of C-O(Å) in $LiKCO_3$, $LiRbCO_3$ and $LiCsCO_3$.

	$LiKCO_3$	$LiRbCO_3$	$LiCsCO_3$
C-O	1.2717	1.2742	1.2726
C-O	1.2891	1.2934	1.2860
C-O	1.3048	1.2973	1.2891
Average bond length	1.2885	1.2883	1.2825
Standard deviation of the C-O bond	0.013	0.010	0.007

TableS5. The calculated refractivity of $LiKCO_3$, $LiRbCO_3$ and $LiCsCO_3$ at static field limit.

	n_x	n_y	n_z
$LiKCO_3$	1.45	1.55	1.57
$LiRbCO_3$	1.49	1.57	1.59
$LiCsCO_3$	1.56	1.61	1.64

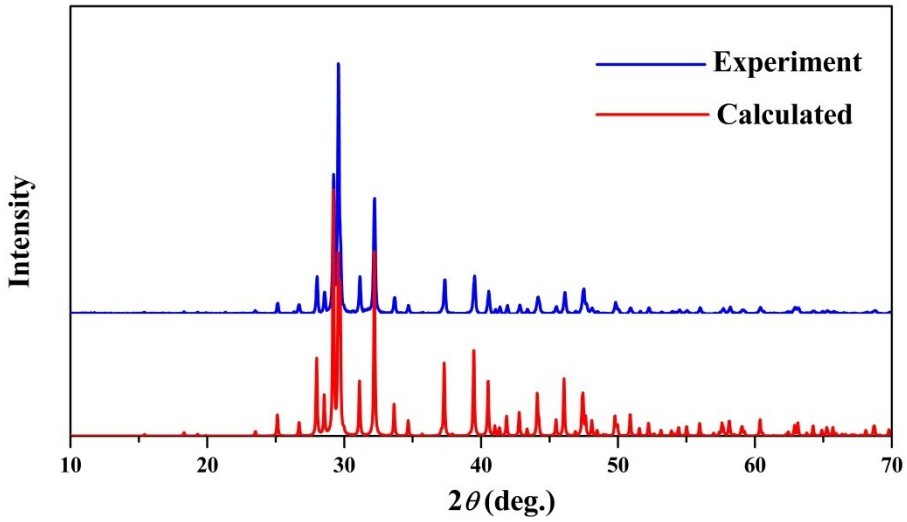


Fig. S1. Powder XRD patterns of $LiKCO_3$.

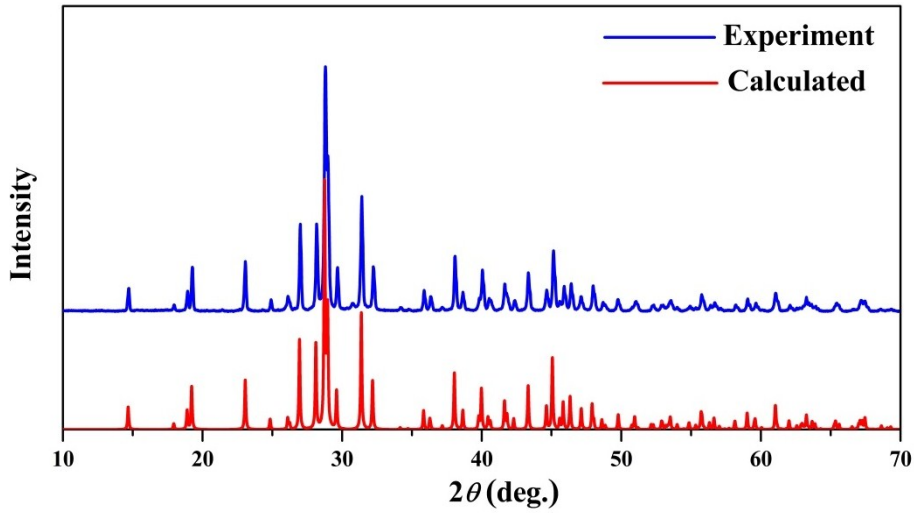


Fig. S2. Powder XRD patterns of $LiRbCO_3$.

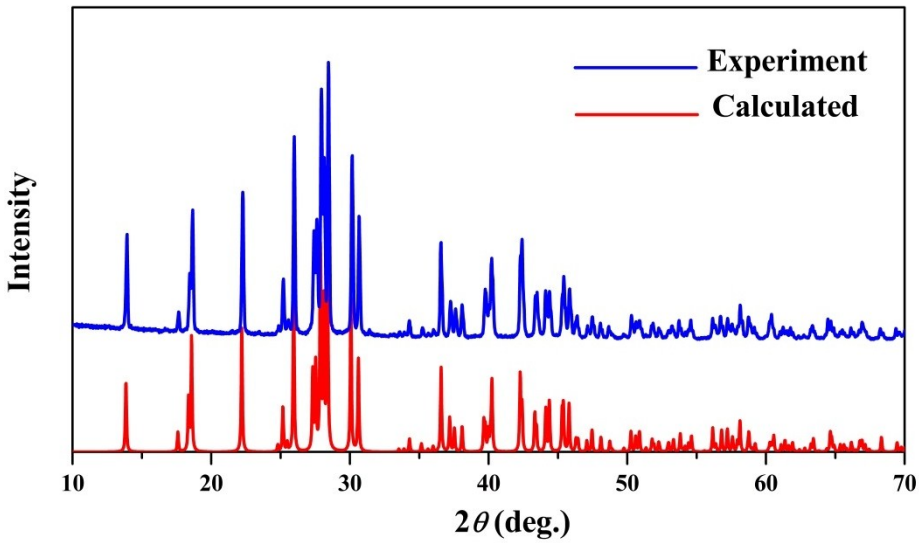
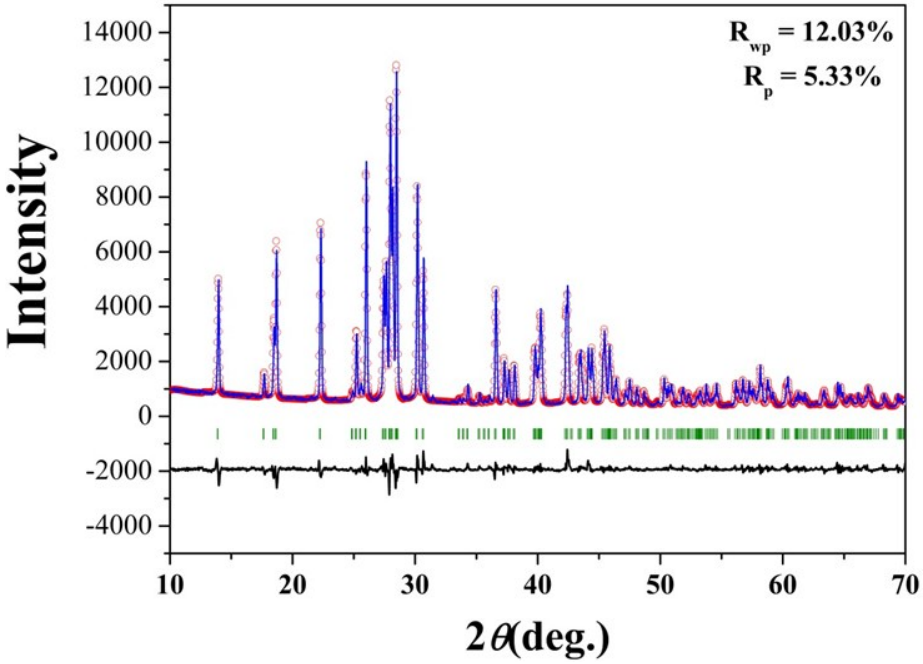


Fig. S3. Powder XRD patterns of $LiCsCO_3$.



FigS4. The Rietveld refinement of $LiCsCO_3$.

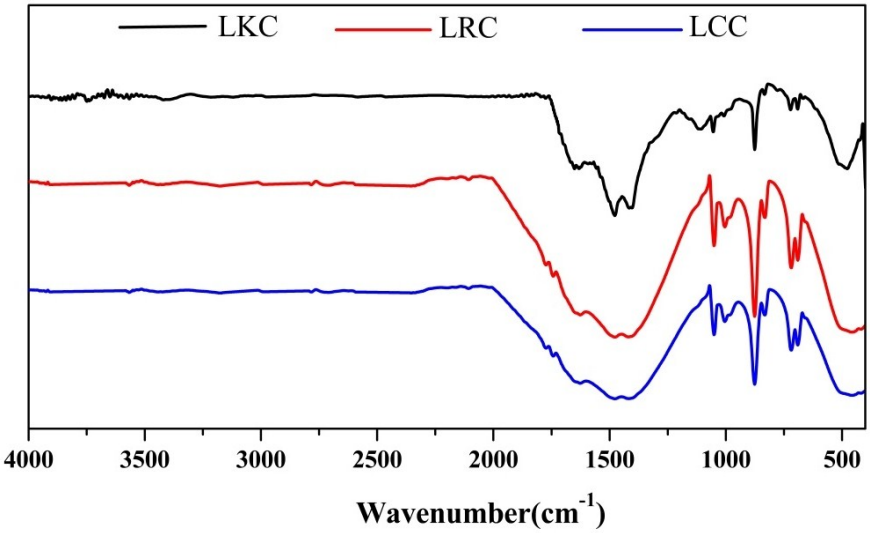


Fig. S5. The IR spectrum of $LiKCO_3$(LKC), $LiRbCO_3$(LRC)and $LiCsCO_3$(LCC).

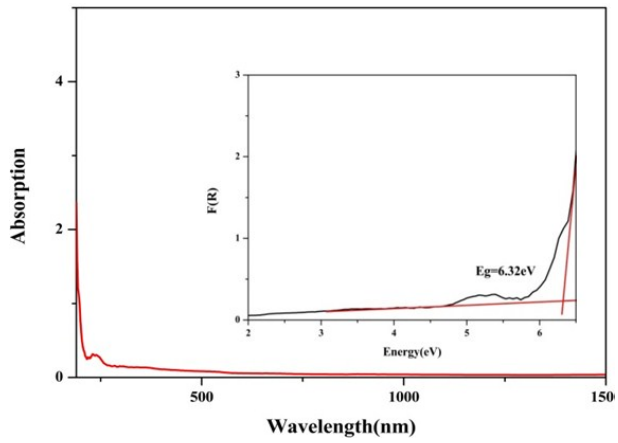


Fig.S6. The UV-vis-NIR Diffuse-Reflectance spectrum of $LiKCO_3$.

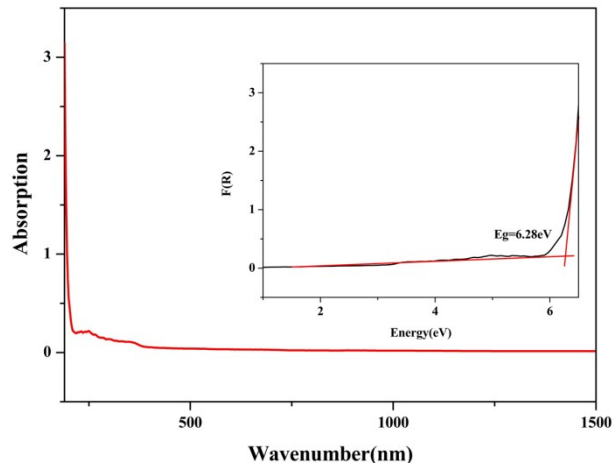


Fig.S7. The UV-vis-NIR Diffuse-Reflectance spectrum of $LiRbCO_3$.

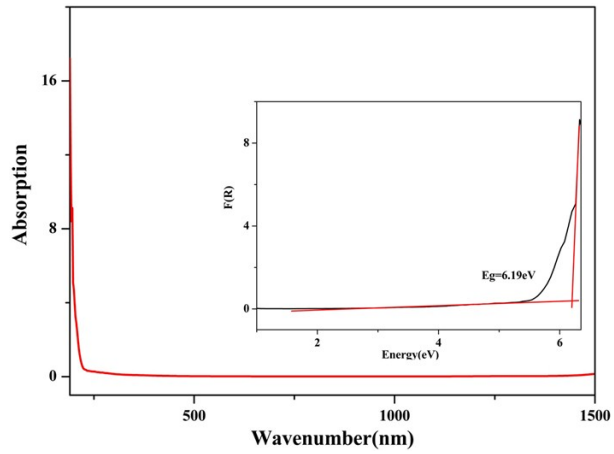


Fig.S8. The UV-vis-NIR Diffuse-Reflectance spectrum of $LiCsCO_3$.

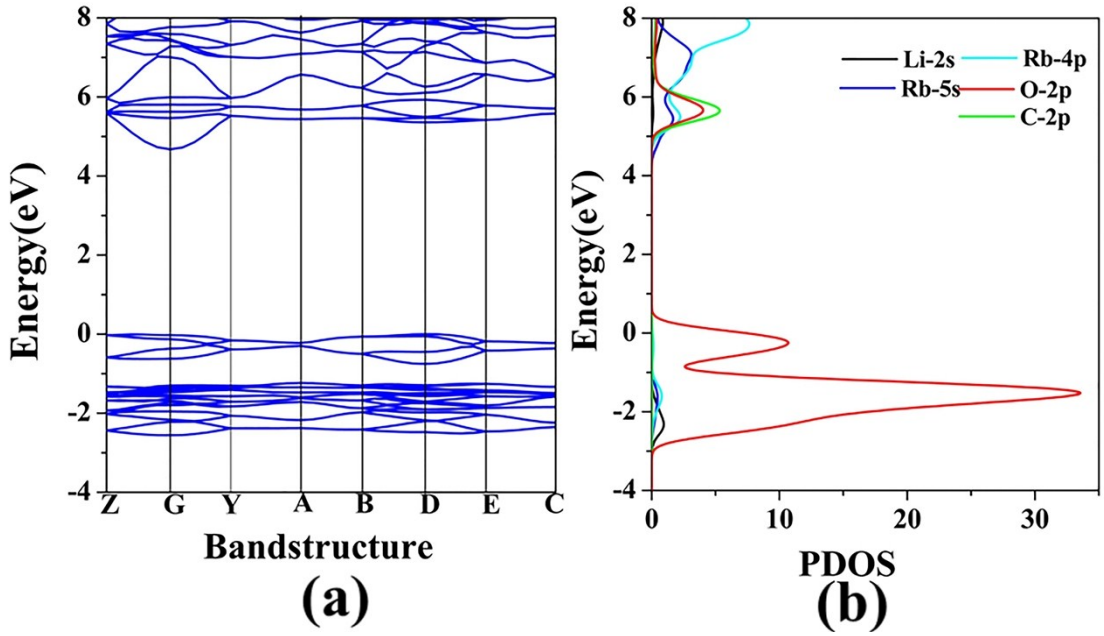


Fig.S9. (a) The band structure of $LiRbCO_3$. (b) The PDOS of $LiRbCO_3$.

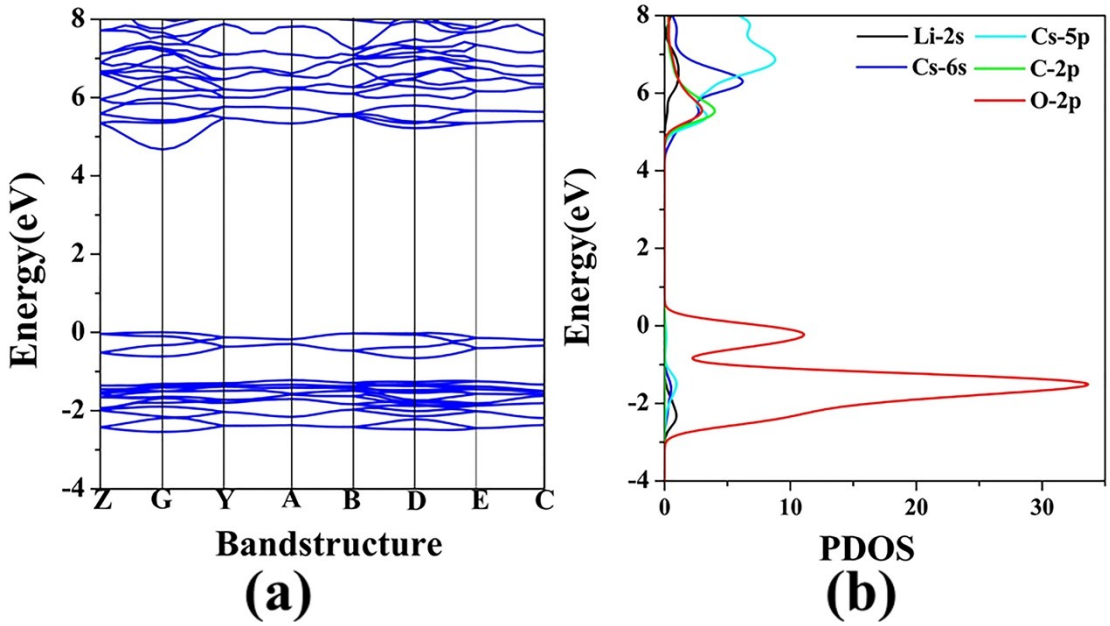


Fig.S10. (a) The band structure of $LiCsCO_3$. (b) The PDOS of $LiCsCO_3$.

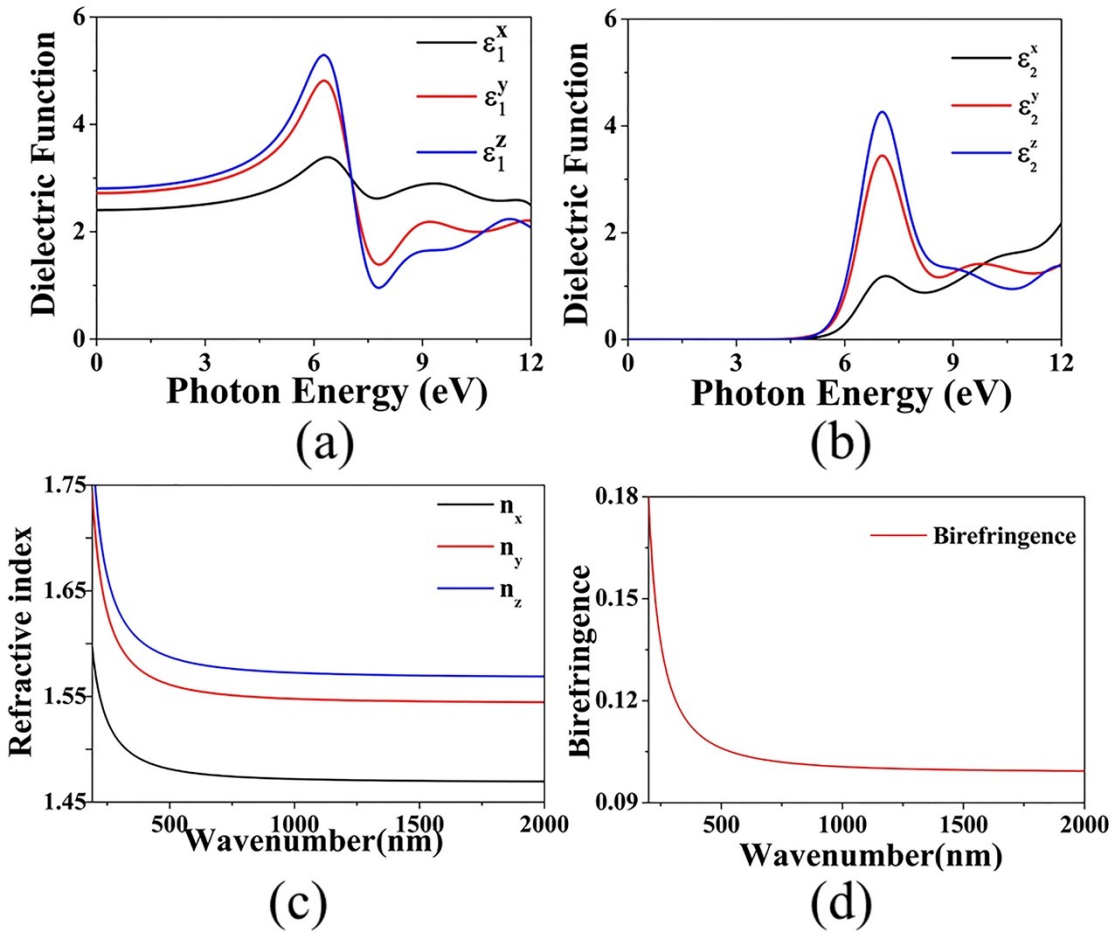


Fig.S11. (a) The real part ε_1 of $LiRbCO_3$. (b) The imaginary part ε_2 of $LiRbCO_3$. (c) The calculated refractive indices of $LiRbCO_3$. (d) The calculated birefringence of $LiRbCO_3$.

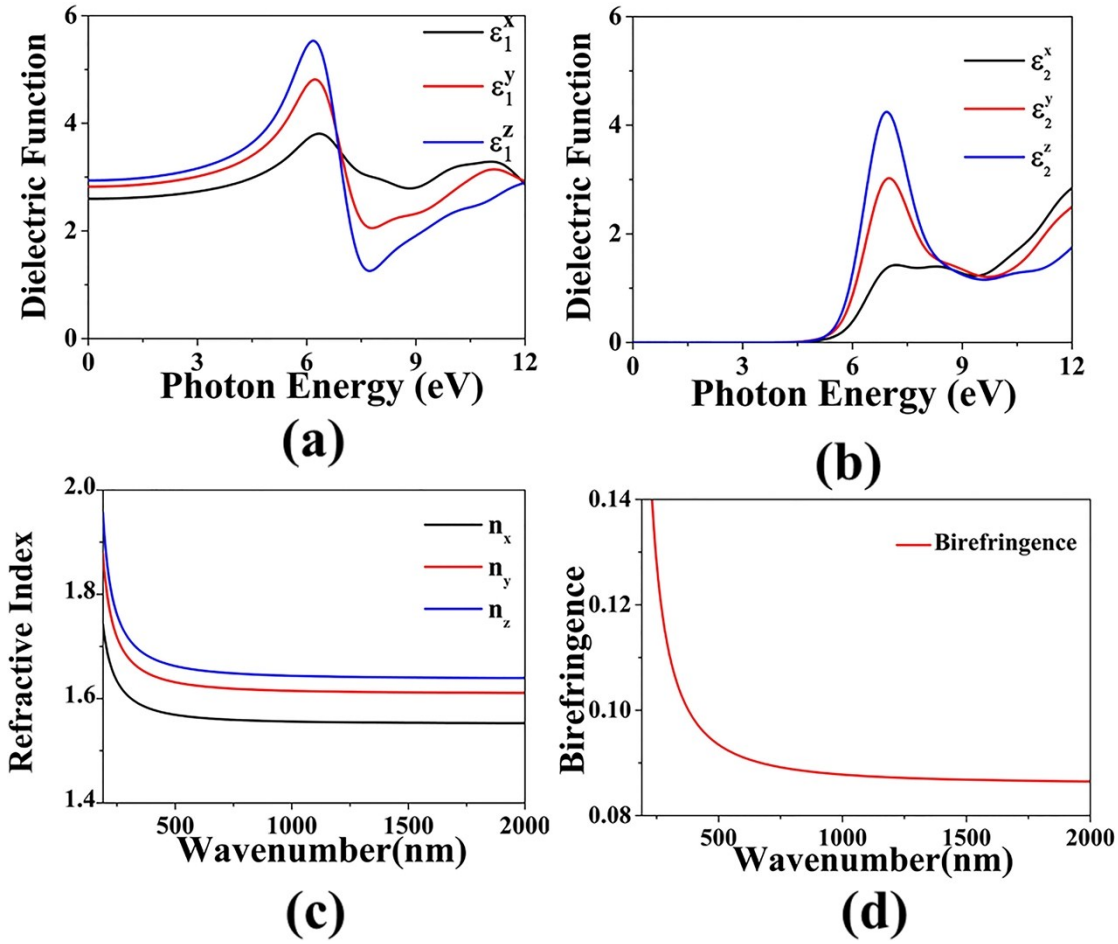


Fig.S12. (a) The real part ε_1 of $LiCsCO_3$. (b) The imaginary part ε_2 of $LiCsCO_3$. (c) The calculated refractive indices of $LiCsCO_3$. (d) The calculated birefringence of $LiCsCO_3$.