Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information (ESI)

$KRE(CO_3)_2$ (RE = Eu, Gd, Tb): New Mixed Metal Carbonates with Strong Photoluminescence and Large Birefringence

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Table S1. Carbonates with experimental and calculated birefringence values reported.

Compound	Space group	Cut-off edge	SHG efficiency (1064 nm)	Birefringence
$LiNaCO_3$[1]	$P1/P\bar{6}/P\bar{6}m2$	-	1.3 × KDP	Experimental: 0.13
$LiKCO_3$[2]	$P2_1/c$	196	-	Calculated:0.11
$LiRbCO_3$[2]	$P2_1/n$	197	-	Calculated:0.10
$LiCsCO_3$[2]	$P2_1/n$	200	-	Calculated:0.09
$KSrCO_3F$[3-6]	$P\bar{6}m2$	< 200	3.33 × KDP	Experimental: 0.1117 (532 nm) Calculated: 0.105 (1064 nm)
$RbSrCO_3F$[3, 4]	$P\bar{6}m2$	< 200	3.33 × KDP	Calculated: 0.102 (1064 nm)
$KCaCO_3F$[3, 4]	$P\bar{6}m2$	< 200	3.61× KDP	Calculated: 0.112 (1064 nm)
$RbCaCO_3F$[3, 4, 7]	$P\bar{6}m2$	< 200	1.11× KDP	Calculated: 0.116 (1064 nm)
$CsCaCO_3F$[3, 4]	$P\bar{6}m2$	< 200	1.11× KDP	Calculated: 0.107 (1064 nm)
$Cs_3Ba_4(CO_3)_3F_5$[3, 4]	$P6_3mc$	210	1.20× KDP	Calculated: 0.034 (1064 nm)
$Ca_2Na_3(CO_3)_3F$[8]	Cm	190	3.00 × KDP	Experimental: 0.082 (532 nm) Calculated: 0.072 (532 nm)
$Y_8O(OH)_{15}(CO_3)_3Cl$[9]	$P6_3$	234	2.5 × KDP	Experimental: 0.092 (1064nm) Calculated: 0.072 (1064 nm)
$RE_8O(CO_3)_3(OH)_{15}X$ (RE = Y, Lu; X = Cl, Br)[10]	$P6_3$	266, 266, 254, 283	1.65/ 2.22/ 1.83/ 3.00 × KDP	Experimental: 0.045/ 0.062/ 0.073/ 0.088 (546.1 nm) Calculated: 0.037/ 0.044/ 0.058/ 0.070 (546.1 nm)
$NaPb_2(CO_3)_2F$[11]	$P6_3/mmc$	289	-	Calculated: 0.269 (1064 nm)
$KPb_2(CO_3)_2F$[7, 12]	$P6_3/mmc$	318	-	Calculated: 0.27 (1064 nm)
$CsPbCO_3F$[5, 7, 13, 14]	$P\bar{6}m2$	299	13.4 × KDP	Calculated: 0.17 (1064 nm)
$RbMgCO_3F$[7, 15]	$P\bar{6}2m$	< 190	160 × α-SiO_2	Calculated: 0.13 (1064 nm)
$RbCdCO_3F$[7, 16]	$P\bar{6}c2$	233	2.8 × KDP	Calculated: 0.12 (1064 nm)
$Cs_3Pb_2(CO_3)_3I$[17]	$C2/m$	300	-	Calculated: 0.14 (546 nm)
$KY(CO_3)_2$[18]	$C2/c$	< 200	-	Calculated: 0.105 (1064 nm)
$Na_2Gd(CO_3)F_3$[18]	$Pbca$	< 200	-	Calculated: 0.084 (1064 nm)
$NaGd_{0.25}Lu_{0.75}(CO_3)F_2$[18]	$Pnma$	< 200	-	Calculated: 0.198 (1064 nm)
$NaY(CO_3)_2$[19]	$P2_1/c$	< 200	-	Calculated: 0.088 (1064 nm)
$YOHCO_3$[19]	$P2_12_12_1$	< 200	2 × KDP	Calculated: 0.077 (1064 nm)
$NaZnCO_3F$[20]	$P\bar{6}2c$	269	2.75 × KDP	Calculated: 0.171 (1064 nm)
$Na_4Zn(CO_3)_3$[20]	$P2_1/c$	305	-	Calculated: 0.138 (1064 nm)
$NaZnCO_3(OH)$[21]	Pc	200	5.2 × KDP	Calculated: 0.114 (1064 nm)
$Zn(NH_3)CO_3$[22]	$Pna2_1$	204	1.5 × KDP	Experimental: 0.087 (546 nm) Calculated：0.085(1064 nm)
$LiZn(OH)CO_3$[23]	$Pmn2_1$	< 190	3.2 × KDP	Calculated：0.147(1064 nm)
$Na_3Zn_2(CO_3)_3F$[24]	$C2/c$	213	-	Calculated：0.11(589 nm)
$Sr_3[SnOSe_3][CO_3]$[25]	$Pmn2_1$	314	1×AGS	Calculated：0.12(1064 nm)
Na_2CO_3[26]	$C2/m$	221	-	Calculated：0.144(1064 nm)
K_2CO_3[26]	$P2_1/c$	225	-	Calculated：0.113(1064 nm)

Rb_2CO_3[26]	$P2_1/c$	237	-	Calculated：0.107(1064 nm)
Cs_2CO_3[26]	$P2_1/c$	328	-	Calculated：0.082(1064 nm)
K_3CO_3F[26]	$R\bar{3}c$	221	-	Calculated：0.085(1064 nm)
$NaHCO_3$[26]	$P2_1/c$	< 190	-	Calculated：0.202(1064 nm)
$KHCO_3$[26]	$P2_1/a$	< 190	-	Calculated：0.172(1064 nm)
$RbHCO_3$[26]	$C\bar{1}$	< 190	-	Calculated：0.164(1064 nm)
$CsHCO_3$[26]	$P2_1/n$	< 190	-	Calculated：0.131(1064 nm)
$K_2HCO_3F·H_2O$[26]	$P2_1/m$	< 190	-	Calculated：0.095(1064 nm)
KLi_2CO_3F[27]	$P6_322$	< 190	-	Calculated: 0.124 (546 nm)

Table S2. Crystallographic data for $KRE(CO_3)_2$ (RE = Eu, Gd, Tb).

Compound	$KEu(CO_3)_2$	$KGd(CO_3)_2$	$KTb(CO_3)_2$
Fw	311.08	316.37	318.04
T (K)	293(2)	293(2)	293(2)
crystal system	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$C2/c$	$C2/c$
a (Å)	8.5882(3)	8.5701(12)	8.5419(7)
b (Å)	9.6029(3)	9.5705(10)	9.5290(6)
c (Å)	6.9976(2)	6.9821(10)	6.9503(5)
β (deg)	111.297(4)	111.291(16)	111.004(9)
V (Å^3)	537.69(3)	533.59(13)	528.14(7)
Z	2	2	2
ρ_{calcd} (g·cm^{-3})	3.843	3.938	4.000
μ (mm^{-1})	12.400	13.170	14.139
R_{int}	0.0477	0.0296	0.1104
GOF on F^2	1.128	1.117	1.079
R1, wR2 ($I > 2\sigma(I)$)[a]	0.0156, 0.0406	0.0173, 0.0406	0.0243, 0.0481
R1, wR2 (all data)	0.0159, 0.0407	0.0178, 0.0408	0.0271, 0.0492

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$; $wR_2 = \{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$.

Table S3. Important bond lengths (Å) for $KEu(CO_3)_2$.

K(1)-O(1)#1	2.793(3)	Eu(1)-O(1)	2.429(3)
K(1)-O(1)#2	2.820(3)	Eu(1)-O(1)#6	2.429(3))
K(1)-O(1)#3	2.793(3)	Eu(1)-O(2)#7	2.358(3)
K(1)-O(1)	2.820(3)	Eu(1)-O(2)	2.532(3)
K(1)-O(2)#4	2.885(3)	Eu(1)-O(2)#6	2.532(3)
K(1)-O(2)#5	2.885(3)	Eu(1)-O(2) #8	2.358(3)
K(1)-O(3)#5	3.123(4)	Eu(1)-O(3) #9	2.313(3)
K(1)-O(3)#4	3.123(4)	Eu(1)-O(3)#4	2.313(3)
K(1)-O(3)#3	3.219(3)	C(1)-O(1)	1.287(5)
K(1)-O(3)#1	3.219(3)	C(1)-O(2)	1.311(5)
		C(1)-O(3)	1.249(5)

Symmetry transformations used to generate equivalent atoms:
[1]+x,1-y,1/2+z; [2]-x,+y,1/2-z; [3]-x,1-y,-z; [4]1/2-x,-1/2+y,1/2-z; [5]-1/2+x,-1/2+y,+z; [6]1-x,+y,1/2-z; [7]1-x,1-y,1-z; [8]+x,1-y,-1/2+z; [9]1/2+x,-1/2+y,+z;

Table S4. Important bond lengths (Å) for $KGd(CO_3)_2$.

K(1)-O(1) #1	2.791(3)	Gd(1)-O(1)#6	2.416(3)
K(1)-O(1)#2	2.816(3)	Gd(1)-O(1)	2.416(3)
K(1)-O(1)#3	2.791(3)	Gd(1)-O(2)#7	2.348(3)
K(1)-O(1)	2.816(3)	Gd(1)-O(2)	2.523(3)
K(1)-O(2)#4	2.878(3)	Gd(1)-O(2) #6	2.523(3)
K(1)-O(2)#5	2.878(3)	Gd(1)-O(2)#8	2.348(3)
K(1)-O(3)#5	3.123(4)	Gd(1)-O(3)#9	2.301(3)
K(1)-O(3)#4	3.123(4)	Gd(1)-O(3)#4	2.301(3))
K(1)-O(3)#3	3.212(3)	C(1)-O(1)	1.274(6)
K(1)-O(3)#1	3.212(3)	C(1)-O(2)	1.315(6)
		C(1)-O(3)	1.256(6)

Symmetry transformations used to generate equivalent atoms:
[1]+x,1-y,1/2+z; [2]-x,+y,1/2-z; [3]-x,1-y,-z; [4]1/2-x,-1/2+y,1/2-z; [5]-1/2+x,-1/2+y,+z; [6]1-x,+y,1/2-z; [7]1-x,1-y,1-z; [8]+x,1-y,-1/2+z; [9]1/2+x,-1/2+y,+z;

Table S5. Important bond lengths (Å) for $KTb(CO_3)_2$.

K(1)-O(1) #1	2.872(3)	Tb(1)-O(1)#4	2.513(3)
K(1)-O(1)#2	2.872(3)	Tb(1)-O(1)	2.335(3)
K(1)-O(2)#3	2.802(3)	Tb(1)-O(1)#8	2.513(3)
K(1)-O(2)#4	2.790(3)	Tb(1)-O(1)#7	2.335(3)
K(1)-O(2)	2.802(3)	Tb(1)-O(2) #7	2.404(3)
K(1)-O(2)#5	2.790(3)	Tb(1)-O(2)	2.404(3)
K(1)-O(3)#6	3.115(4)	Tb(1)-O(3)	2.288(3)
K(1)-O(3)#7	3.115(4)	Tb(1)-O(3) #7	2.288(3)
K(1)-O(3) #2	3.223(3)	C(1)-O(1)# 8	1.307(5)
K(1)-O(3) #1	3.223(3)	C(1)-O(2)# 7	1.268(5)
		C(1)-O(3)#9	1.262(5)

Symmetry transformations used to generate equivalent atoms:
[1]-1/2+x,1/2-y,1/2+z; [2]-1/2-x,1/2-y,-z; [3]-1-x,+y,1/2-z; [4]+x,1-y,1/2+z; [5]-1-x,1-y,-z; [6]-1+x,+y,+z; [7]-x,+y,1/2-z; [8]-x,1-y,-z; [9]1/2-x,1/2+y,1/2-z

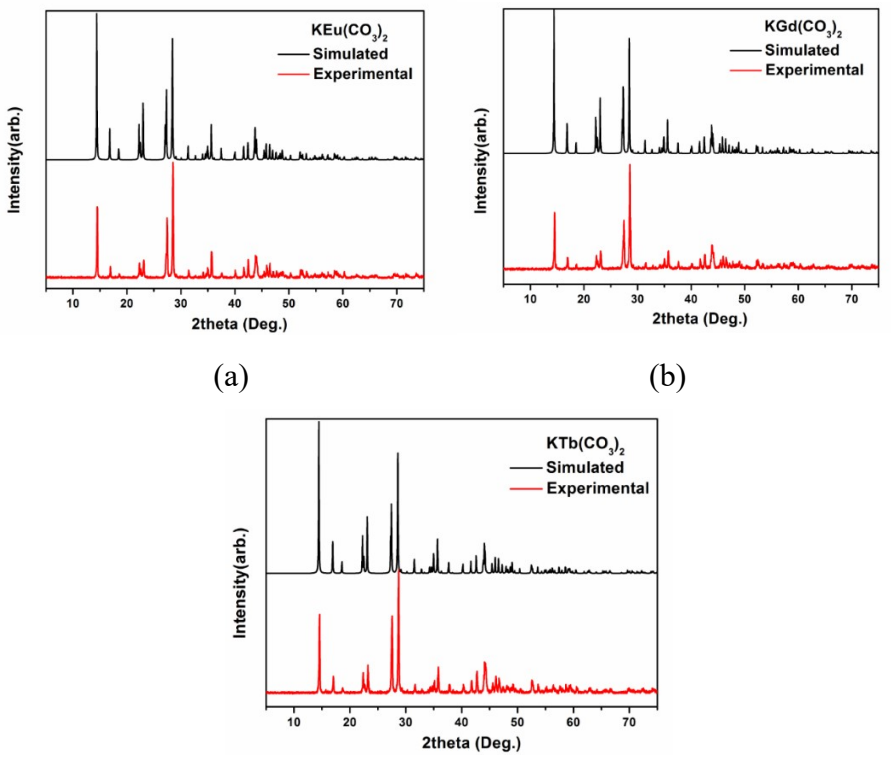


Figure S1. Experimental and simulated powder X-ray diffraction patterns of $KRE(CO_3)_2$ (RE = Eu (a), Gd (b), Tb (c)).

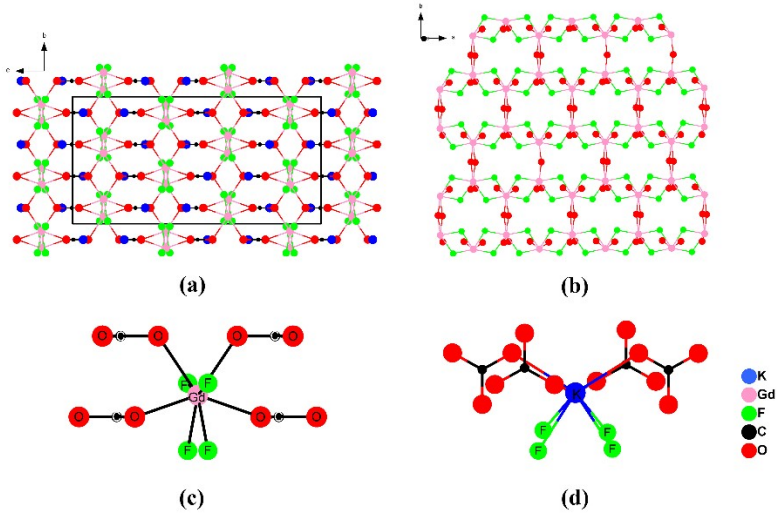


Figure S2. Structure of $KGdCO_3F_2$: View of the three-dimensional structure of $KGdCO_3F_2$ down the *a* axis (a), the two-dimensional $[GdO_4F_4]^{9-}$ layer within the *ab* plane (b), coordination environment around the Gd1 atom (c) and K1 atom (d).

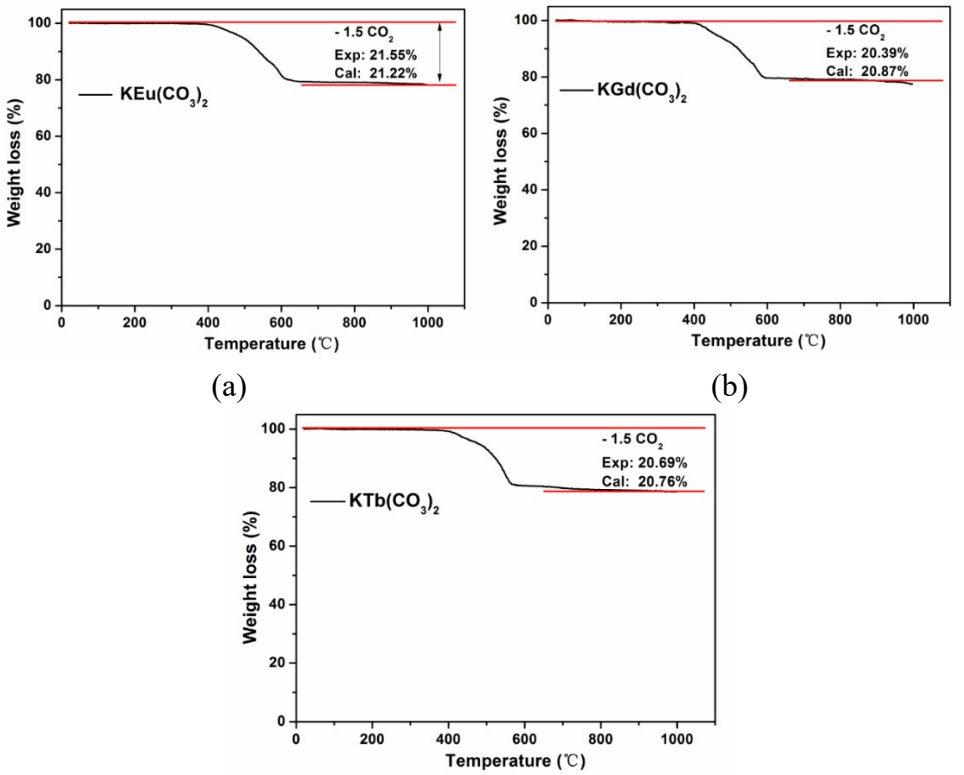


Figure S3. TGA curves of $KRE(CO_3)_2$ (RE = Eu (a), Gd (b), Tb (c)).

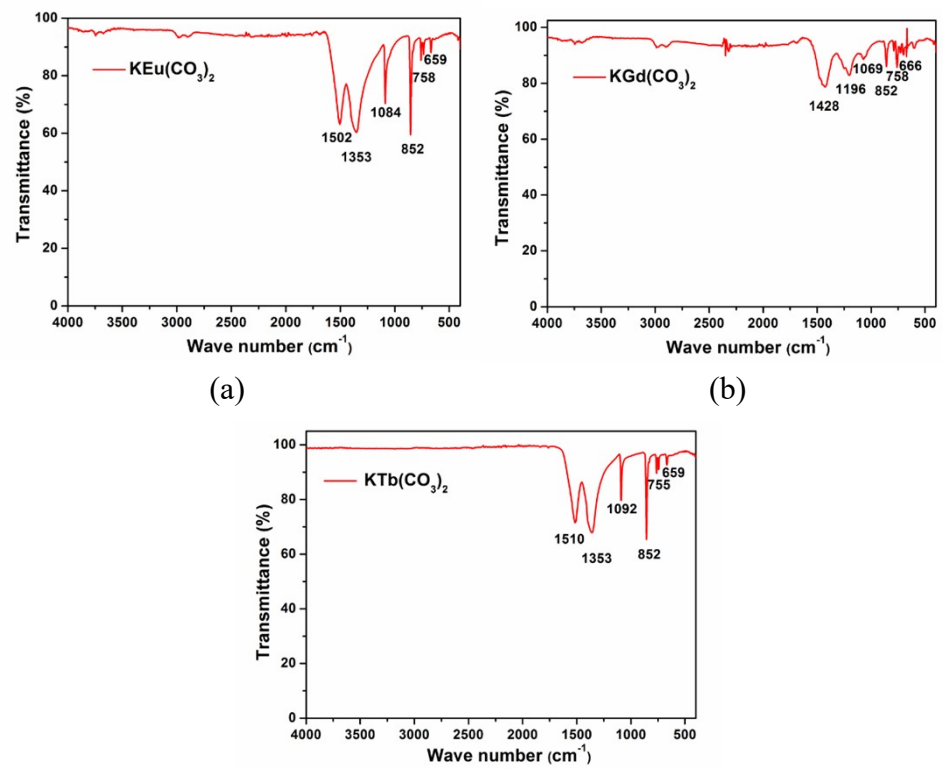
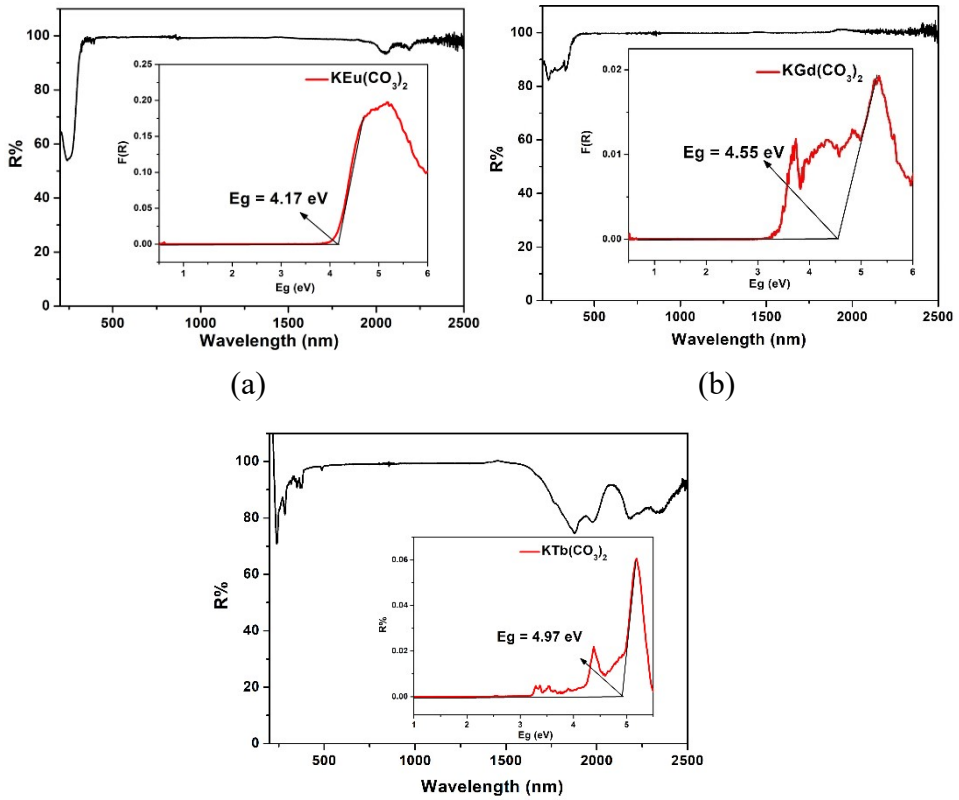


Figure S4. IR spectra of $KRE(CO_3)_2$ (RE = Eu (a), Gd (b), Tb (c)).



(a) (b)

(c)

Figure S5. The UV-visible-near IR diffuse reflectance spectra of $KRE(CO_3)_2$ (RE = Eu (a), Gd (b), Tb (c)).

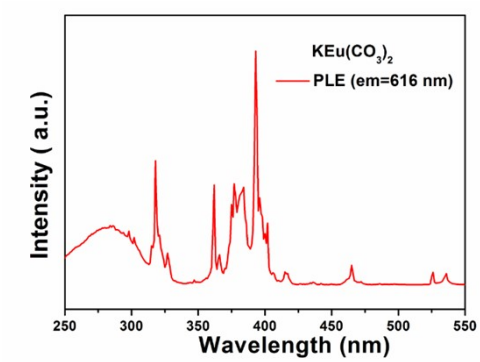
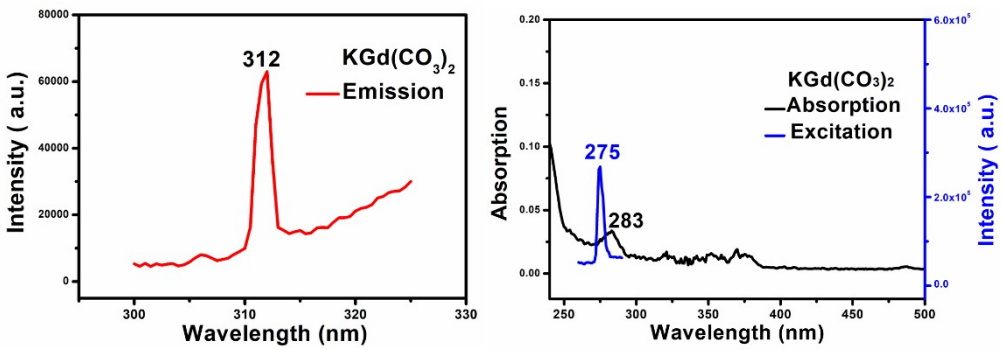


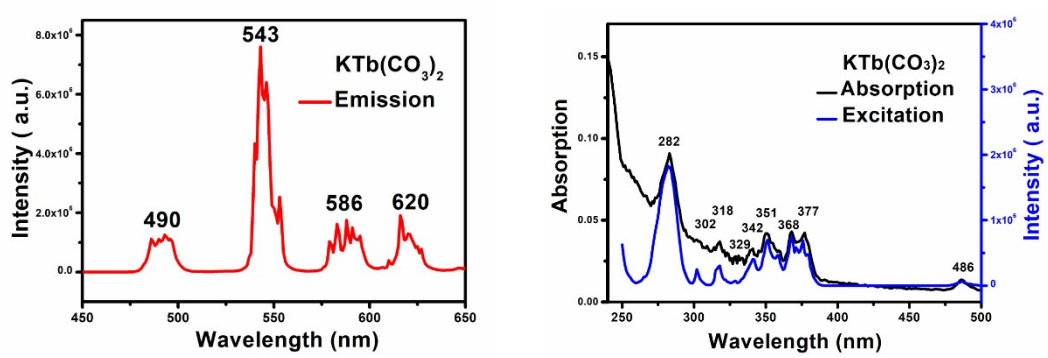
Figure S6. The excitation spectrum of $KEu(CO_3)_2$ under emission at 616 nm.



(a) (b)

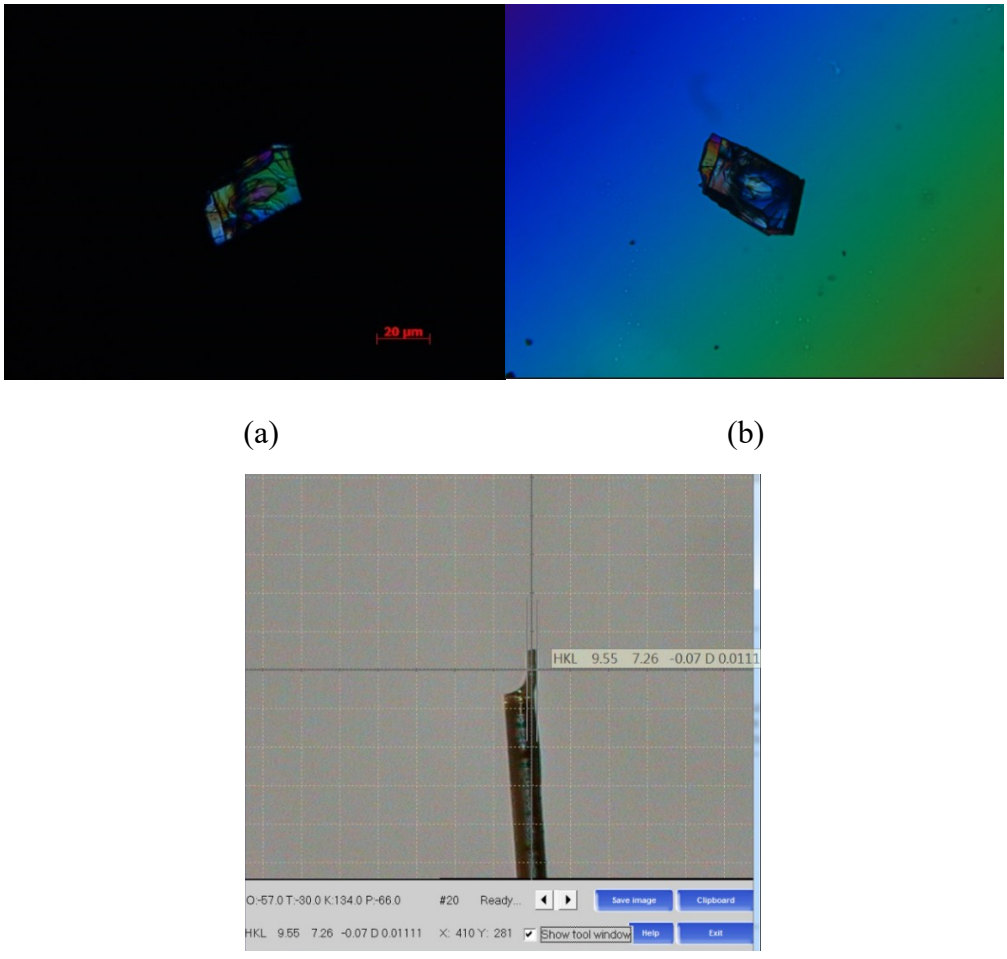
Figure S7. The photoluminescence spectra (PL, red line) of $KGd(CO_3)_2$ at 275 nm excitation (a);

absorption spectra (black line) and photoluminescence excitation spectra (PLE, blue line) at 312 nm emission of $KGd(CO_3)_2$ (b).



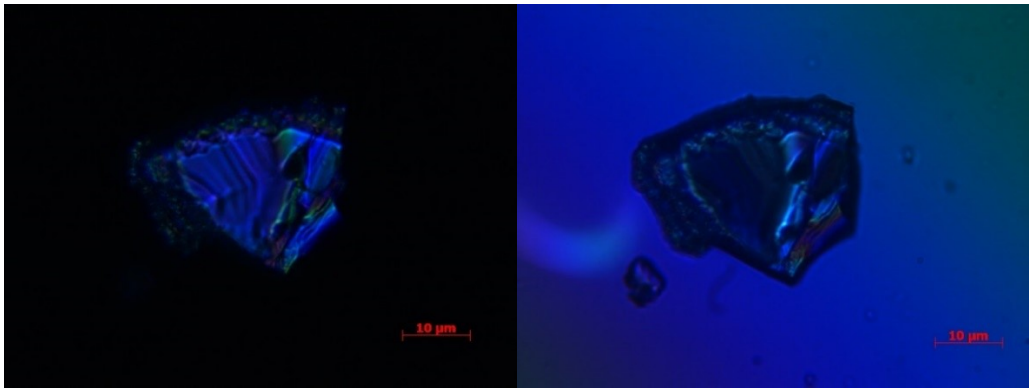
(a) (b)

Figure S8. The photoluminescence spectra (PL, red line) of $KTb(CO_3)_2$ at 282 nm excitation (a); absorption spectra (black line) and photoluminescence excitation spectra (PLE, blue line) at 543 nm emission of $KTb(CO_3)_2$ (b).

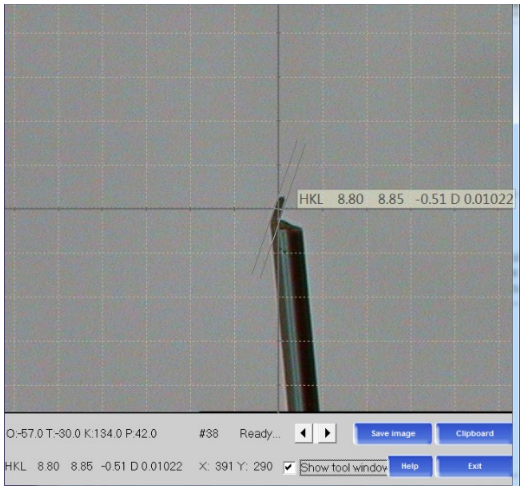


(c)

Figure S9. Photographs of $KEu(CO_3)_2$ for the measurement of birefringence: the original crystal (a), the complete extinction crystal (b) and the thickness of the crystal (c).



(a) (b)



(c)

Figure S10. Photographs of $KGd(CO_3)_2$ for the measurement of birefringence: the original crystal (a), the complete extinction crystal (b) and the thickness of the crystal (c).

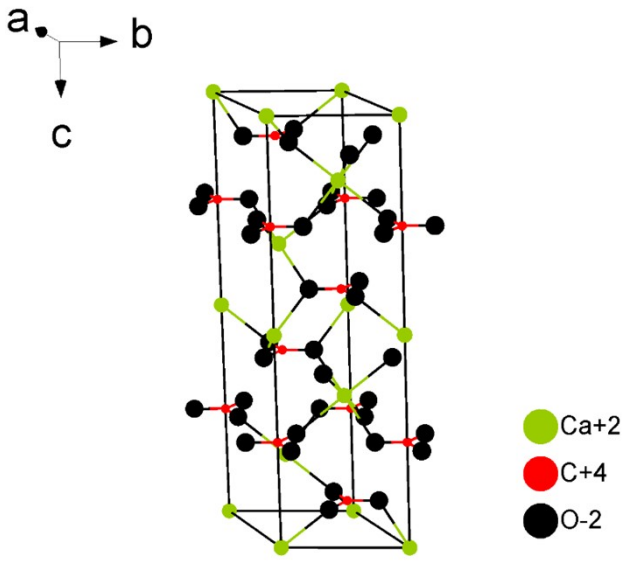
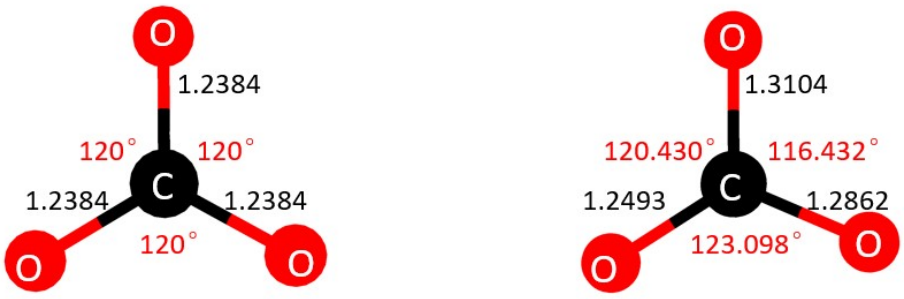
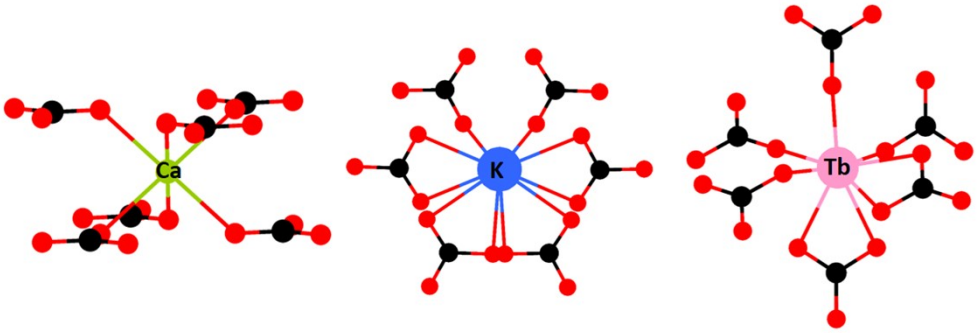


Figure S11. The structure of $CaCO_3$.



(a) (b)

Figure S12. The structure of CO_3 in $CaCO_3$ (a) and $KTb(CO_3)_2$ (b).



(a) (b) (c)

Figure S13. The CaO_6 octahedron (a) in $CaCO_3$, KO_{10} polyhedron (b) and TbO_8 polyhedron (c) in $KTb(CO_3)_2$.

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