Electronic Supplementary Information

Yunxia Song,[a,b] Min Luo,[a,*] Dan Zhao,[c] Guang Peng,[a,b] Chensheng Lin,[a] and Ning Ye[a,*]

a. Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, P. R. China

b. University of Chinese Academy of Sciences, Beijing 100049, P. R. China

c. Department of Physics and Chemistry, Henan Polytechnic University, Jiaozuo, Henan 454000, China

Email: lm8901@fjirsm.ac.cn
nye@fjirsm.ac.cn

Table S1. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters (A^2x10^3) for $Na_6Ca_5(CO_3)_8$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	Y	z	$U_{eq}(Å^2)$
Ca(1)	10000	10000	6379(4)	20(1)
Ca(2)	11483(3)	8517(3)	4587(5)	49(1)
Na(2)	11483(3)	8517(3)	4587(5)	49(1)
Ca(3)	9944(2)	4972(1)	5739(3)	21(1)
Na(1)	11843(2)	8157(2)	7512(3)	5(1)
Na(3)	13333	6667	3293(15)	95(5)
C(1)	13333	6667	5676(17)	21(4)
C(2)	14822(7)	9645(15)	8505(10)	27(3)
C(3)	8327(6)	6653(12)	6177(9)	19(2)
C(4)	10000	10000	8605(16)	20(5)
O(1)	12598(4)	7402(4)	5655(7)	23(2)
O(2)	7606(4)	5211(9)	6107(8)	31(2)
O(3)	13804(8)	9790(8)	8964(6)	42(2)
O(4)	14586(5)	9173(9)	7522(7)	29(2)
O(5)	9806(6)	7401(6)	6192(6)	24(1)
Na(3)	13333	6667	3293(15)	95(5)
O(6)	10000	10000	9581(16)	45(5)
O(7)	10594(14)	11190(30)	8120(20)	72(17)
O(8)	11160(40)	10580(20)	8060(30)	110(20)

Table S2. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters (A^2x10^3) for $Na_2Ca_2(CO_3)_3$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	Y	z	$U_{eq}(Å^2)$
Ca(1)	0	2832(1)	4979(1)	12(1)
Na(1)	-5000	5000	4293(3)	16(1)
Na(2)	0	0	6154(3)	16(1)
O(1)	-5000	1981(2)	771(4)	19(1)
O(2)	-2747(3)	3457(2)	2180(3)	14(1)
C(1)	-5000	2952(3)	1720(5)	11(1)
O(3)	0	0	437(5)	17(1)
O(4)	0	1013(2)	3129(4)	18(1)
C(2)	0	0	2273(7)	11(1)

Table S3. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters (A^2x10^3) for $Na_2Ca(CO_3)_2$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	Y	z	$U_{eq}(Å^2)$
Ca(1)	3784(1)	2043(1)	7229(1)	15(1)
Na(1)	1053(1)	592(2)	5827(1)	24(1)
Na(2)	6486(1)	594(2)	6113(1)	28(1)
C(1)	3747(2)	-1281(4)	7216(3)	14(1)
C(2)	3859(3)	2530(3)	4945(2)	15(1)
O(1)	4821(2)	-528(3)	7168(2)	21(1)
O(2)	2606(2)	-589(3)	7203(2)	20(1)
O(3)	3761(2)	-2751(3)	7294(2)	17(1)
O(4)	4829(2)	2954(3)	5567(2)	25(1)
O(5)	3593(2)	3339(3)	4096(2)	27(1)
O(6)	3177(2)	1374(2)	5217(2)	27(1)

Table S4. Bond lengths (Å) for $Na_6Ca_5(CO_3)_8$

Ca(1)-O(6)#1	2.266(19)	C(2)-O(4)	1.306(15)
Ca(1)-O(8)	2.35(4)	C(2)-Ca(3)#16	2.828(13)
Ca(1)-O(8)#2	2.35(4)	C(2)-Na(1)#10	2.884(8)
Ca(1)-O(8)#3	2.35(4)	C(3)-O(2)	1.261(13)
Ca(1)-O(7)	2.43(3)	C(3)-O(5)#4	1.290(7)
Ca(1)-O(7)#3	2.43(3)	C(3)-O(5)	1.290(7)
Ca(1)-O(7)#2	2.43(3)	C(3)-Ca(3)#17	2.929(6)
Ca(1)-O(5)#4	2.537(5)	C(4)-O(7)#2	1.20(3)
Ca(1)-O(5)#3	2.537(5)	C(4)-O(7)#3	1.20(3)
Ca(1)-O(5)#2	2.537(5)	C(4)-O(7)	1.20(3)
Ca(1)-O(5)#5	2.537(5)	C(4)-O(8)#3	1.22(4)
Ca(1)-O(5)	2.537(5)	C(4)-O(8)#2	1.22(4)
Ca(2)-O(1)	2.365(9)	C(4)-O(8)	1.22(4)
Ca(2)-O(3)#6	2.381(7)	C(4)-O(6)	1.23(3)
Ca(2)-O(3)#7	2.381(7)	C(4)-Ca(2)#16	2.868(10)
Ca(2)-O(8)#6	2.49(4)	C(4)-Na(2)#16	2.868(10)
Ca(2)-O(5)#8	2.512(8)	C(4)-Ca(2)#18	2.868(10)
Ca(2)-O(5)	2.512(8)	C(4)-Na(2)#18	2.868(10)
Ca(2)-O(6)#1	2.587(5)	O(1)-Ca(3)#10	2.570(2)
Ca(2)-C(4)#1	2.868(10)	O(2)-Ca(3)#17	2.527(3)
Ca(2)-O(7)#9	2.913(19)	O(3)-Na(2)#16	2.381(7)
Ca(2)-O(7)#6	2.913(19)	O(3)-Ca(2)#16	2.381(7)
Ca(2)-Ca(3)	3.424(4)	O(3)-Ca(3)#16	2.496(8)
Ca(2)-Ca(3)#10	3.424(4)	O(4)-Ca(3)#10	2.375(10)
Ca(3)-O(4)#11	2.375(10)	O(4)-Na(1)#10	2.419(3)

Ca(3)-O(3)#6	2.496(8)	Na(3)-Na(2)#10	3.616(10)
Ca(3)-O(3)#12	2.496(8)	Na(3)-Ca(2)#10	3.616(10)
Ca(3)-O(2)	2.527(3)	Na(3)-Na(2)#11	3.616(10)
Ca(3)-O(2)#13	2.527(3)	Na(3)-Ca(2)#11	3.616(10)
Ca(3)-O(1)	2.570(2)	Na(3)-Ca(3)#10	4.271(14)
Ca(3)-O(1)#11	2.570(2)	Na(3)-Ca(3)#11	4.271(14)
Ca(3)-O(5)	2.582(5)	Na(3)-Ca(3)#19	4.305(15)
Ca(3)-O(5)#14	2.582(5)	Na(3)-Ca(3)#1	4.305(15)
Ca(3)-C(2)#6	2.828(13)	O(6)-Ca(1)#16	2.266(19)
Ca(3)-C(3)	2.929(6)	O(6)-Na(2)#18	2.587(5)
Ca(3)-C(3)#13	2.929(6)	O(6)-Ca(2)#16	2.587(5)
Na(1)-O(7)#3	2.31(2)	O(6)-Na(2)#16	2.587(5)
Na(1)-O(4)	2.419(3)	O(6)-Ca(2)#18	2.587(5)
Na(1)-O(4)#11	2.419(3)	O(6)-Ca(2)#20	2.587(5)
Na(1)-O(5)	2.448(7)	O(6)-Na(2)#20	2.587(5)
Na(1)-O(5)#8	2.448(7)	O(7)-O(8)#2	1.03(2)
Na(1)-O(3)	2.590(8)	O(7)-O(8)	1.03(2)
Na(1)-O(3)#8	2.590(8)	O(7)-O(7)#2	1.79(4)
Na(1)-O(1)	2.685(9)	O(7)-O(7)#3	1.79(4)
Na(1)-C(2)	2.884(8)	O(7)-Na(1)#2	2.31(2)
Na(1)-C(2)#11	2.884(8)	O(7)-Ca(2)#16	2.913(19)
Na(1)-O(8)#3	2.930(14)	O(7)-Na(2)#16	2.913(19)
Na(1)-O(8)	2.930(13)	O(7)-Na(2)#20	2.913(19)
C(1)-O(1)	1.283(6)	O(7)-Ca(2)#20	2.913(19)
C(1)-O(1)#11	1.283(7)	O(8)-O(7)#3	1.03(2)
C(1)-O(1)#10	1.283(7)	O(8)-O(8)#3	1.75(6)
C(1)-Ca(3)#10	2.957(2)	O(8)-O(8)#2	1.75(6)
C(1)-Ca(3)#11	2.957(2)	O(8)-Na(2)#16	2.49(4)
C(1)-Na(3)	3.00(3)	O(8)-Ca(2)#16	2.49(4)
C(2)-O(3)#15	1.249(9)	O(8)-Na(1)#2	2.930(13)
C(2)-O(3)	1.249(9)		

Symmetry transformations used to generate equivalent atoms:

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

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

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

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

#10 -x+y+2,-x+2,z #11 -y+2,x-y,z

#12 y,x-1,z-1/2 #13 -x+y+1,-x+1,z

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

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

#19 -x+2,-y+1,z-1/2 #20 -x+2,-y+2,z+1/2

Table S5. Bond lengths (Å) for $Na_2Ca_2(CO_3)_3$

O(1)-C(1)	1.269(4)
O(2)-C(1)	1.295(3)
C(1)-O(2)#1	1.295(3)
O(3)-C(2)	1.308(6)
O(4)-C(2)	1.277(4)
C(2)-O(4)#2	1.277(4)

Symmetry transformations used to generate equivalent atoms:

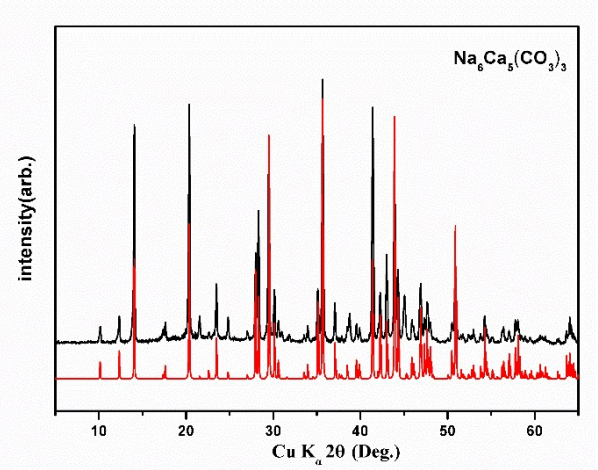
#1 -x-1,y,z #2 -x,-y,z

Table S6. Bond lengths (Å) for $Na_2Ca(CO_3)_2$

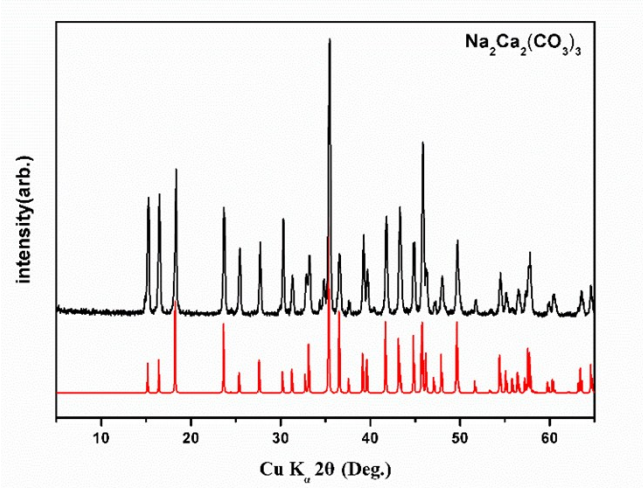
Ca(1)-O(5)#1	2.315(2)	Na(2)-Ca(1)#10	3.3229(15)
Ca(1)-O(4)	2.422(2)	Na(2)-Na(1)#9	3.580(2)
Ca(1)-O(1)	2.479(2)	Na(2)-Ca(1)#11	3.7189(17)
Ca(1)-O(2)#2	2.498(2)	Na(2)-Na(1)#10	3.766(2)
Ca(1)-O(3)#3	2.5396(17)	C(1)-O(1)	1.265(3)
Ca(1)-O(3)#2	2.5629(17)	C(1)-O(3)	1.289(4)
Ca(1)-O(2)	2.589(2)	C(1)-O(2)	1.296(3)
Ca(1)-O(6)	2.601(2)	C(1)-Ca(1)#5	2.934(3)
Ca(1)-O(1)#3	2.649(2)	C(1)-Ca(1)#11	2.959(3)
Ca(1)-C(2)	2.826(3)	C(2)-O(6)	1.266(3)
Ca(1)-C(1)	2.908(4)	C(2)-O(5)	1.284(3)
Ca(1)-C(1)#2	2.934(3)	C(2)-O(4)	1.290(3)
Na(1)-O(3)#2	2.314(3)	C(2)-Na(1)#2	2.889(3)
Na(1)-O(6)	2.361(2)	C(2)-Na(1)#8	2.905(3)
Na(1)-O(4)#4	2.456(2)	C(2)-Na(2)#9	3.044(3)
Na(1)-O(4)#5	2.492(3)	O(1)-Ca(1)#11	2.649(2)
Na(1)-O(2)	2.515(3)	O(1)-Na(1)#10	2.915(3)
Na(1)-O(5)#4	2.643(3)	O(2)-Ca(1)#5	2.498(2)
Na(1)-C(2)#5	2.889(3)	O(2)-Na(2)#6	2.564(3)
Na(1)-C(2)#4	2.905(3)	O(3)-Na(1)#5	2.314(3)
Na(1)-O(5)#5	2.914(3)	O(3)-Na(2)#11	2.439(3)
Na(1)-O(1)#6	2.915(3)	O(3)-Ca(1)#11	2.5396(17)
Na(1)-Na(1)#7	3.104(3)	O(3)-Ca(1)#5	2.5629(17)
Na(2)-O(5)#8	2.327(2)	O(4)-Na(1)#8	2.456(2)
Na(2)-O(1)	2.329(3)	O(4)-Na(1)#2	2.492(3)
Na(2)-O(6)#9	2.392(3)	O(5)-Ca(1)#12	2.315(2)
Na(2)-O(3)#3	2.439(3)	O(5)-Na(2)#4	2.327(2)
Na(2)-O(2)#10	2.564(3)	O(5)-Na(1)#8	2.643(3)
Na(2)-O(4)	2.734(3)	O(5)-Na(1)#2	2.914(3)
Na(2)-C(2)#9	3.044(3)	O(6)-Na(2)#9	2.392(3)

Table S7. The contribution of different geometrical factors (g) for structure factors (C)

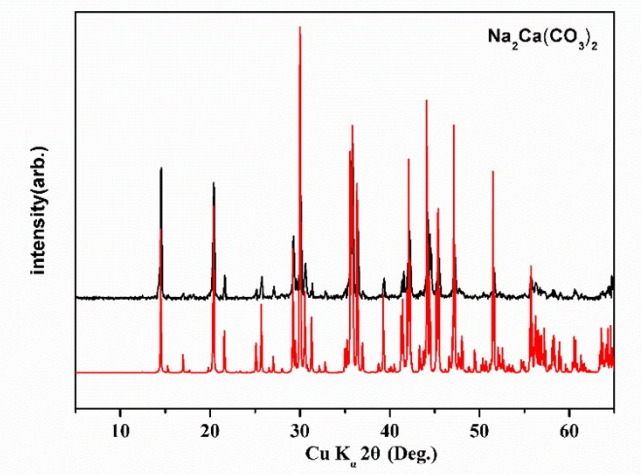
Crystals(n)	$g_{311/n}$	$g_{322/n}$	$g_{333/n}$
$Na_6Ca_5(CO_3)_8$ (n=2)	0.133	-	0.196
$Na_2Ca_2(CO_3)_3$ (n=2)	0.355	0.079	0.434



(a)

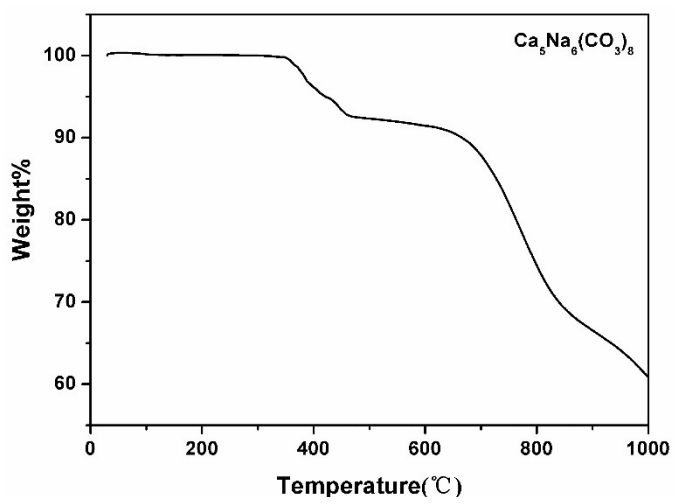


(b)

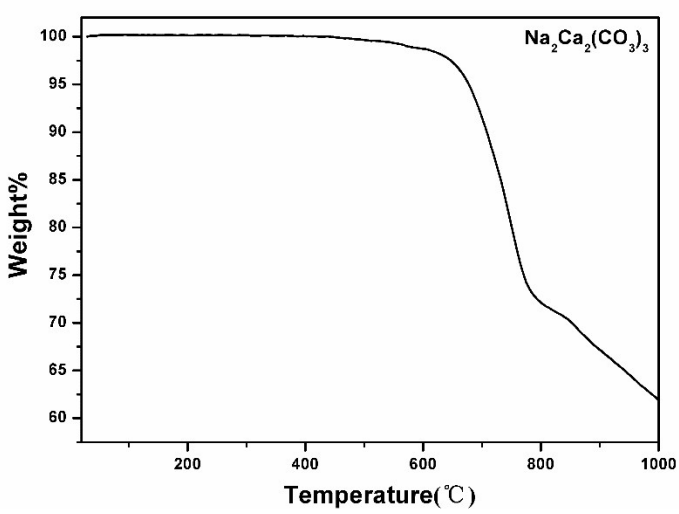


(c)

Figure S1. X-ray powder diffraction patterns of $Na_6Ca_5(CO_3)_8$, $Na_2Ca_2(CO_3)_3$ and $Na_2Ca(CO_3)_2$ (**black colour** is crystal sample; **red colour** is simulation results)



(a)



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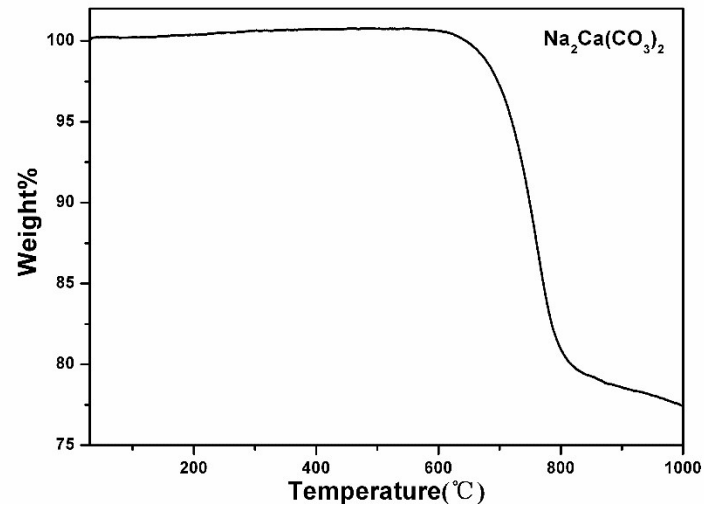


(c)

Figure S2. TG curves of (a) $Na_6Ca_5(CO_3)_8$, (b) $Na_2Ca_2(CO_3)_3$ and (c) $Na_2Ca(CO_3)_2$.

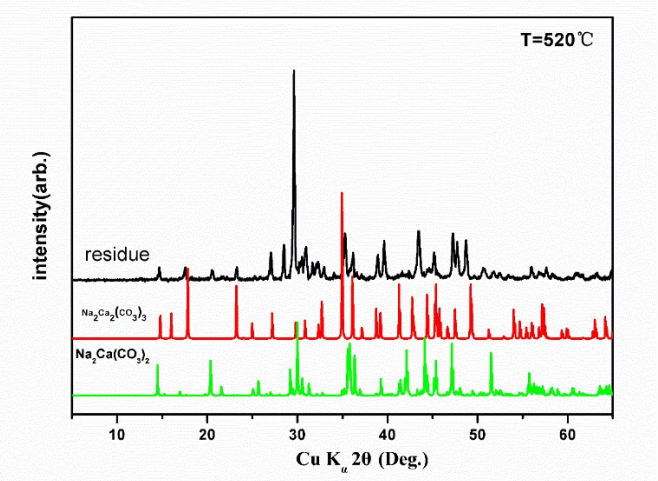


Figure S3. X-ray powder diffraction patterns of $Na_6Ca_5(CO_3)_8$ at 520℃.

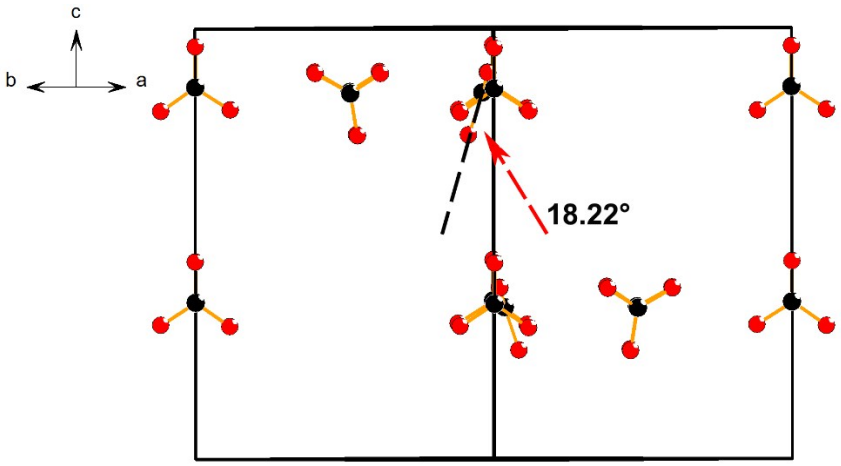


Figure S4. The standing-on-edge $[CO_3]^{2-}$ groups in $Na_6Ca_5(CO_3)_8$

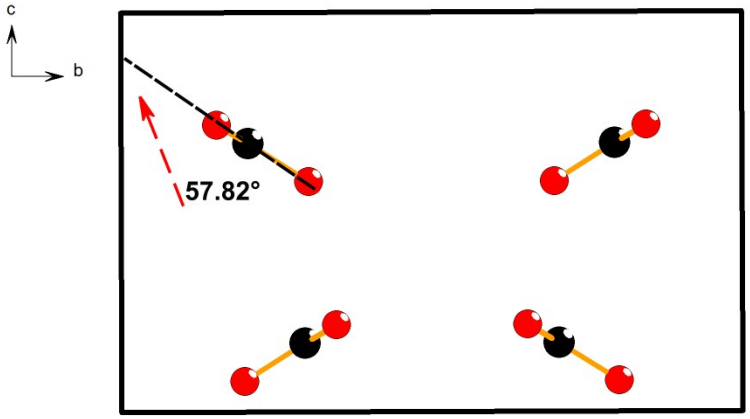
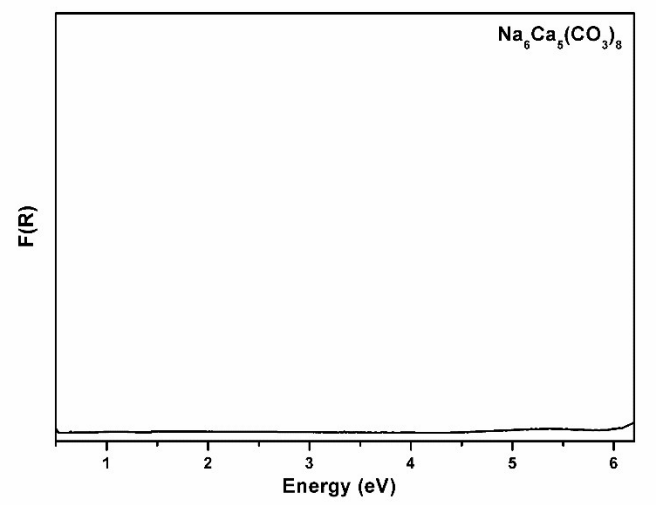
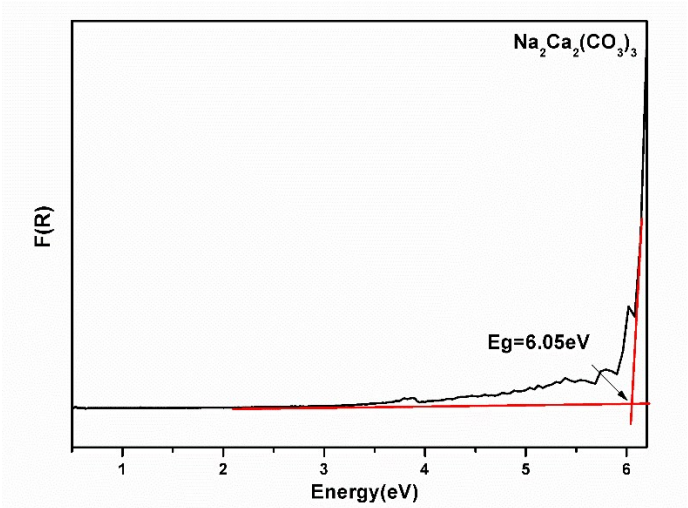


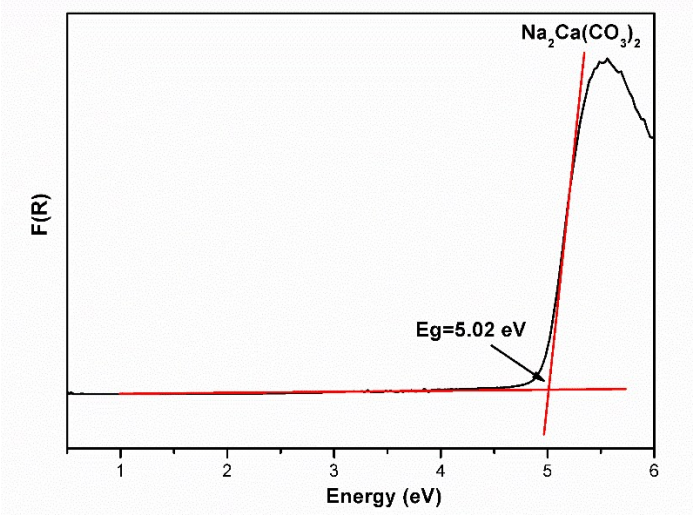
Figure S5. The standing-on-edge $[CO_3]^{2-}$ groups in $Na_2Ca_2(CO_3)_3$



(a)

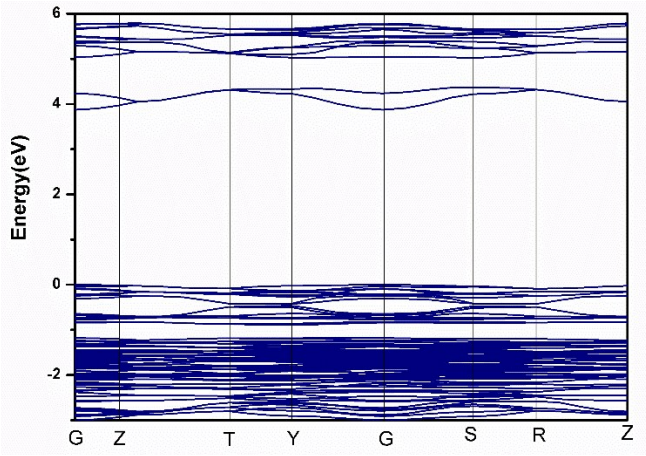


(b)

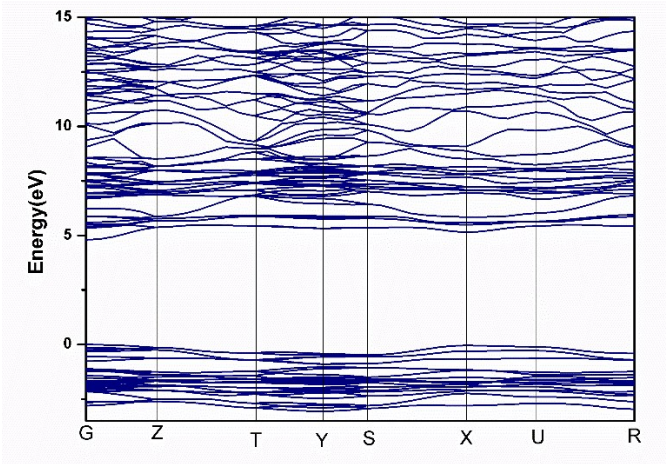


(c)

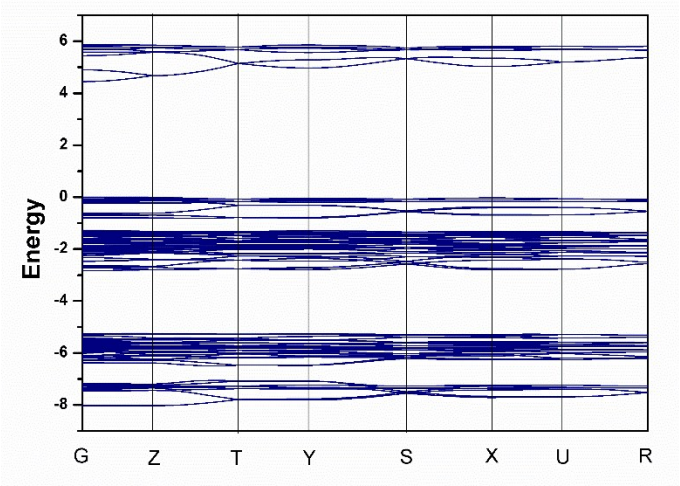
Figure S6 Diffuse reflectance absorption curves of the powder samples of (a) $Na_6Ca_5(CO_3)_8$, (b) $Na_2Ca_2(CO_3)_3$ and (c) $Na_2Ca(CO_3)_2$



(a)



(b)



(c)

Figure S7. The calculated band structures for (a) $Na_6Ca_5(CO_3)_8$, (b) $Na_2Ca_2(CO_3)_3$ and (c) $Na_2Ca(CO_3)_2$

The Anionic Group Theory Calculation.

The macroscopic second-order susceptibility $\chi^{(2)}$ could be expressed by Eq. 3 according to the anionic group theory.

$$x_{ijk}^{(2)} = \frac{F}{V}\sum_{\mathrm{p}}\sum_{\mathrm{i'j'k'}}\alpha_{\mathrm{ii'}}\alpha_{\mathrm{jj'}}\alpha_{\mathrm{kk'}}\beta_{\mathrm{i'j'k'}}^{(2)}(\mathrm{P}), \quad (1)$$

where F is the correction factor of the localized field, V is the volume of the unit cell,$\alpha_{ii'}$, $\alpha_{jj'}$, and $\alpha_{kk'}$ are the direction cosines between the macroscopic coordinates axes of the crystal and the microscopic coordinates axes of [CO_3] or [BO_3] groups, and $\beta_{i'j'k'}$ is the microscopic second-order susceptibility tensors of an individual group, which can be calculated with quantum chemistry method.

Because [CO_3] and [BO_3] is a planar group in point group D_{3h}, in the Kleinman approximation, there are only two nonvanishing second-order susceptibility $\beta_{111}^{(2)} = -\beta_{122.}^{(2)}$ .The geometrical factor, g, could be derived from Eq. (1). and Eq. (2) could be simplified according to the deduction process[44]:

$$x_{\mathrm{ijk}}^{(2)} = \frac{F}{V}\cdot \mathrm{g}_{\mathrm{ijk}}\cdot\beta_{111}^{(2)} \quad (2)$$

$g=\max(g_{ijk})$; (i,j,k=1,2,3) (3)

In case of unspontaneous polarization, the structural criterion C is defined as:

$$C = \frac{g}{n} \quad (4)$$

where n is the number of anionic groups in a unit cell.