Electronic Supplementary Information (ESI)

Exploration of new UV nonlinear optical materials in the sodium-zinc fluoride carbonates system with the discovery of a new regulation mechanism for the arrangement of $[CO_3]^{2-}$ groups

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Methods

Calculation of bond valence

The bond valence have been calculated using the formula

$$V_i = \sum_j S_{ij} = \sum_j \exp\{(r_0 - r_{ij}) / B\} \quad (1)$$

where S_{ij} is the bond valence associated with bond length r_{ij}. Parameters r_0 and B (usually 0.37) are empirically determined parameters.[1,2]

Calculation of structural criterion (*C*)

The contribution of anionic groups $[CO_3]^{2-}$ to the whole SHG coefficient can be calculated by calculating the structural criterion (*C*) based on the anionic group theory.[3] The macroscopic second-order susceptibility $\chi^{(2)}$ could be expressed by equation (2),

$$\chi_{ijk}^{(2)} = \frac{F}{V} \sum_P \sum_{i'j'k'} \alpha_{ii'} \alpha_{jj'} \alpha_{kk'} \beta_{i'j'k'}^{(2)}(P) \qquad P = [CO_3]^{2-} \quad (2)$$

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 of the crystal and the microscopic coordinates of $[CO_3]^{2-}$ groups, and $\beta_{i'j'k'}^{(2)}(P)$ is the microscopic second-order susceptibility tensor of an individual group. Owing to the fact that $[CO_3]^{2-}$ is a planar group in point group D_{3h}, there are only two nonvanishing second-order susceptibilities $\beta_{111}^{(2)} = \beta_{222}^{(2)}$ in the Kleinman approximation. Because the geometrical factor, g, can be derived from equation (2), equation (2) may be simplified according to the deduction process shown in ref. 4:

$$\chi_{ijk}^{(2)} = \frac{F}{V} \cdot g_{ijk} \cdot \beta_{111}^{(2)}([CO_3]) \quad (3)$$

$$g_{ijk} = \sum_P^n [\alpha(i1)\alpha(j1)\alpha(k1) - \alpha(i1)\alpha(j2)\alpha(k2) - \alpha(i2)\alpha(j1)\alpha(k2) - \alpha(i2)\alpha(j2)\alpha(k1)] \quad (4)$$

$$g = \max(g_{ijk})(i, j, k = 1, 2, 3) \quad (5)$$

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

$$C = \frac{g}{n} \quad (6)$$

where *n* is the number of $[CO_3]^{2-}$ groups in a unit cell. Thus, the $\chi_{ijk}^{(2)}$ is proportional to the monocelled number density of the $[CO_3]^{2-}$ groups (*n/V*) and the structural criterion (*C*).

The space group of $NaZnCO_3F$ belonging to class -6m2, which has only one independent tensors of second-order susceptibility, namely $\chi_{222}^{(2)}$. Therefore, the Eq.(4) could be further simplified into the Eq.(7) below:

$$g_{222} = \sum_P^n [\alpha(21)\alpha(21)\alpha(21) - 3\alpha(21)\alpha(22)\alpha(22)] \quad (7)$$

Where α(21) and α(22) are the are the direction cosines between the macroscopic coordinate y axis of the crystal and the microscopic coordinate x' and y' axis of $[CO_3]^{2-}$ groups, respectively. As shown in Figure S1, θ and Φ were defined as the relative rotation angle of $[CO_3]^{2-}$ groups and the angle between x and x' axis, respectively. The quantity relations among them are the following:

$$\alpha(21) = \cos(90^o - \phi) = \sin\phi;\ \alpha(22) = \cos\phi$$

$$\phi = 30^o - \frac{1}{2}\theta \quad (8)$$

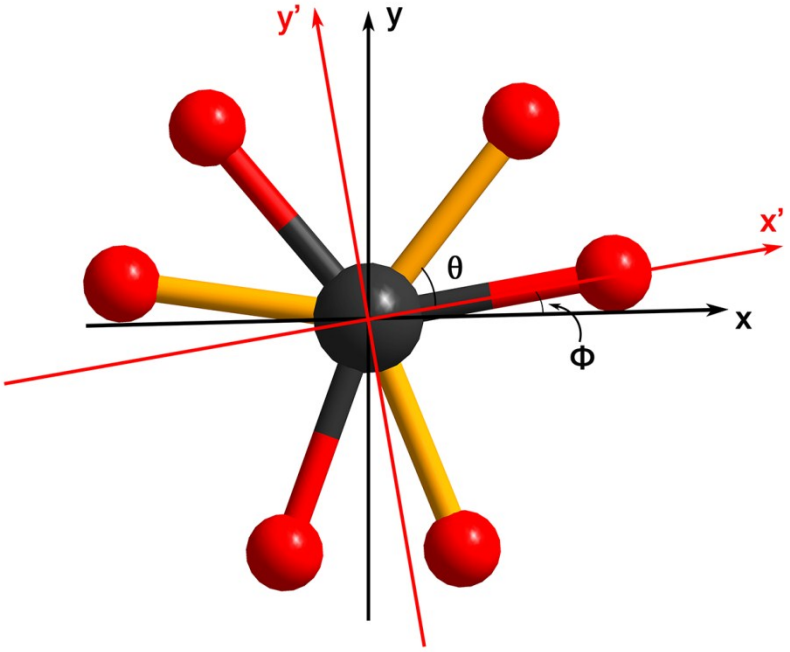

Figure S1. Microscopic coordinates (x-y) of the crystal and the microscopic coordinates (x'-y') of the $[CO_3]^{2-}$ groups.

Thus, the g_{222} can be expressed as the following Eq.(9):

$$g_{222} = \sin^3\phi - 3\cos^2\phi\sin\phi = -\sin 3\phi = -\cos(3\theta/2) \quad (9)$$

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

$$C = \frac{g}{n} = \frac{|g_{222}|}{2} = \cos(3\theta/2) \quad (10)$$

In consideration of the two types rotational angle (θ), namely 41.820° (θ1) and 43.962° (θ2), the averaging of *C* was calculated as following process:

$$C = \frac{1}{3}\cos(3\times 41.82^o/2) + \frac{2}{3}\cos(3\times 43.962^o/2) = 0.424$$

Table S1. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for $NaZnCO_3F$

Atom	x	y	z	U(eq)
Zn(1)	3390(1)	3320(1)	1247(1)	10(1)
Na(1)	3542(5)	204(5)	2500	20(1)
Na(2)	0	2931(4)	0	19(1)
O(1)	2292(5)	4922(5)	1323(2)	21(1)
O(2)	1733(5)	627(5)	1472(2)	15(1)
O(3)	6056(5)	4451(5)	932(2)	17(1)
F(1)	4216(6)	3596(7)	2500	22(1)
F(2)	2616(6)	2616(6)	0	21(1)
C(1)	0	0	1472(5)	8(2)
C(2)	6667	3333	931(5)	12(2)
C(3)	3333	6667	1313(6)	13(2)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S2. Selected bond lengths (Å) and angles (degrees) for $NaZnCO_3F$

Zn(1)-O(1)	1.990(4)	F(1)#5-Na(1)-O(1)#1	89.23(16)
Zn(1)-O(2)	2.018(4)	O(2)-Na(1)-O(1)#1	72.18(13)
Zn(1)-O(3)	2.018(3)	O(2)#6-Na(1)-O(1)#1	130.36(19)
Zn(1)-F(2)	2.0375(16)	O(3)#10-Na(2)-O(2)#11	154.78(13)
Zn(1)-F(1)	2.0432(15)	O(2)#11-Na(2)-O(2)#3	122.68(19)
Na(1)-F(1)#5	2.262(6)	F(2)-Na(2)-O(1)#12	130.32(10)
Na(1)-O(2)	2.358(4)	O(1)#1-Na(1)-O(1)#7	89.4(2)
Na(1)-O(2)#6	2.358(4)	F(1)#5-Na(1)-F(1)	101.5(3)
Na(1)-O(1)#1	2.600(4)	O(2)-Na(1)-F(1)	68.79(14)
Na(1)-O(1)#7	2.600(4)	O(1)#1-Na(1)-F(1)	134.33(10)
Na(1)-F(1)	2.628(6)	F(1)#5-Na(1)-O(3)#8	64.58(11)
Na(1)-O(3)#8	2.866(4)	O(2)-Na(1)-O(3)#8	143.91(17)
Na(1)-O(3)#5	2.866(4)	O(2)#6-Na(1)-O(3)#8	69.81(11)
Na(2)-F(2)	2.354(3)	O(1)#1-Na(1)-O(3)#8	143.90(15)
Na(2)-F(2)#3	2.354(3)	O(1)#7-Na(1)-O(3)#8	67.07(11)
Na(2)-O(3)#9	2.414(4)	F(1)-Na(1)-O(3)#8	77.81(11)
Na(2)-O(3)#10	2.414(4)	F(1)#5-Na(1)-O(3)#5	64.58(11)
Na(2)-O(2)#11	2.661(4)	O(2)-Na(1)-O(3)#5	69.81(11)
Na(2)-O(2)#3	2.661(4)	O(3)#8-Na(1)-O(3)#5	116.62(18)
Na(2)-O(1)#12	2.748(4)	F(2)-Na(2)-F(2)#3	108.8(3)
Na(2)-O(1)	2.748(4)	F(2)-Na(2)-O(3)#9	88.53(12)
O(1)-C(3)	1.284(4)	F(2)#3-Na(2)-O(3)#9	139.93(10)
O(2)-C(1)	1.284(3)	O(3)#9-Na(2)-O(3)#10	101.1(2)
O(3)-C(2)	1.282(3)	F(2)-Na(2)-O(2)#11	65.21(10)
O(1)-Zn(1)-O(2)	117.37(15)	F(2)#3-Na(2)-O(2)#11	81.99(12)
O(1)-Zn(1)-O(3)	118.79(15)	O(3)#9-Na(2)-O(2)#11	72.81(11)
O(2)-Zn(1)-O(3)	123.82(14)	F(2)#3-Na(2)-O(1)#12	69.83(11)
O(1)-Zn(1)-F(2)	93.70(11)	O(3)#9-Na(2)-O(1)#12	71.50(12)
O(2)-Zn(1)-F(2)	84.04(16)	O(3)#10-Na(2)-O(1)#12	89.30(14)
O(3)-Zn(1)-F(2)	91.50(15)	O(1)#10-C(3)-O(1)	119.99(2)
O(1)-Zn(1)-F(1)	96.53(18)	O(1)#10-C(3)-O(1)#4	119.99(2)
O(2)-Zn(1)-F(1)	88.15(17)	O(1)-C(3)-O(1)#4	119.98(2)
O(3)-Zn(1)-F(1)	86.64(16)	O(2)#1-C(1)-O(2)#3	120.000(3)
F(2)-Zn(1)-F(1)	169.19(17)	O(2)#1-C(1)-O(2)	120.001(3)
F(1)#5-Na(1)-O(2)	134.38(12)	O(2)#3-C(1)-O(2)	119.999(3)
O(2)-Na(1)-O(2)#6	85.3(2)	O(3)#2-C(2)-O(3)#5	120.000(2)
O(2)#11-Na(2)-O(1)#12	65.50(11)	O(3)#2-C(2)-O(3)	120.000(3)
O(2)#3-Na(2)-O(1)#12	131.57(12)	O(3)#5-C(2)-O(3)	120.000(2)
O(1)#12-Na(2)-O(1)	149.9(2)		

Symmetry transformations used to generate equivalent atoms:

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

#7 -x+y,-x,-z+1/2 #8 -y+1,x-y,-z+1/2 #9 x-y,-y+1,-z #10 -x+y,-x+1,z #11 y,x,-z #12 -x,-x+y,-z

Table S3. Anisotropic displacement parameters ($Å^2×10^3$) for $NaZnCO_3F$

The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2hka^* b^* U12]$

	U11	U22	U33	U23	U13	U12
Zn(1)	9(1)	9(1)	13(1)	0(1)	0(1)	4(1)
Na(1)	17(2)	29(2)	23(2)	0	0	17(2)
Na(2)	20(2)	16(1)	22(2)	3(1)	6(1)	10(1)
O(1)	15(2)	11(2)	36(2)	-2(2)	0(2)	6(2)
O(2)	10(2)	14(2)	20(2)	0(1)	-2(2)	5(2)
O(3)	13(2)	12(2)	28(2)	5(2)	5(2)	7(2)
F(1)	18(2)	24(3)	13(2)	0	0	2(2)
F(2)	27(2)	27(2)	14(2)	0(1)	0(1)	16(2)
C(1)	7(2)	7(2)	10(4)	0	0	4(1)
C(2)	11(3)	11(3)	12(4)	0	0	6(1)
C(3)	11(3)	11(3)	18(4)	0	0	5(1)

Table S4. Atomic coordinates ($×10^4$) and equivalent isotropic displacement parameters ($Å^2×10^3$) for $Na_4Zn(CO_3)_3$

Atom	x	y	z	U(eq)
Zn(1)	7986(1)	5336(1)	6928(1)	14(1)
Na(1)	2741(2)	3730(1)	6106(1)	17(1)
Na(2)	2987(2)	4831(1)	8724(1)	21(1)
Na(3)	12302(2)	2381(1)	8418(1)	24(1)
Na(4)	2361(2)	7789(1)	4409(1)	28(1)
O(1)	1740(3)	5252(1)	6408(2)	15(1)
O(2)	5321(3)	6014(1)	5898(2)	16(1)
O(3)	6336(3)	4280(1)	7400(2)	17(1)
O(4)	1213(3)	6447(1)	5275(2)	20(1)
O(5)	10288(3)	3721(1)	8049(2)	21(1)
O(6)	5330(3)	5983(1)	9439(2)	20(1)
O(7)	7385(3)	7239(1)	9348(2)	22(1)
O(8)	6668(3)	2900(1)	7793(2)	28(1)
O(9)	9044(3)	6140(1)	8332(2)	31(1)
C(1)	2709(4)	5916(1)	5854(2)	12(1)
C(2)	7220(4)	6449(1)	9058(2)	14(1)
C(3)	7794(4)	3618(1)	7763(2)	14(1)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S5. Selected bond lengths (Å) and angles (degrees) for $Na_4Zn(CO_3)_3$

Zn(1)-O(3)	1.9262(16)	Na(4)-O(7)#12	2.506(2)
Zn(1)-O(2)	1.9725(16)	Na(4)-O(9)#13	2.575(2)
Zn(1)-O(1)#1	1.9750(16)	Na(4)-O(8)#3	2.590(2)
Zn(1)-O(9)	1.9771(18)	Na(4)-O(8)#14	2.915(3)
Na(1)-O(3)	2.3462(19)	O(1)-C(1)	1.296(2)
Na(1)-O(2)#3	2.3645(19)	O(2)-C(1)	1.308(2)
Na(1)-O(4)#4	2.390(2)	O(3)-C(3)	1.315(3)
Na(1)-O(7)#5	2.392(2)	O(4)-C(1)	1.252(3)
Na(1)-O(5)#6	2.404(2)	O(5)-C(3)	1.273(3)
Na(1)-O(1)	2.4690(18)	O(6)-C(2)	1.271(3)
Na(1)-O(8)	2.869(2)	O(7)-C(2)	1.280(3)
Na(2)-O(6)	2.2598(19)	O(8)-C(3)	1.262(3)
Na(2)-O(5)#6	2.2898(19)	O(9)-C(2)	1.302(3)
Na(2)-O(3)	2.3742(18)	O(3)-Zn(1)-O(2)	108.61(7)
Na(2)-O(6)#8	2.407(2)	O(3)-Zn(1)-O(1)#1	115.66(6)
Na(2)-O(1)	2.532(2)	O(2)-Zn(1)-O(1)#1	120.61(6)
Na(2)-O(9)#6	2.859(2)	O(3)-Zn(1)-O(9)	117.80(8)
Na(3)-O(5)	2.3580(19)	O(2)-Zn(1)-O(9)	101.42(8)
Na(3)-O(7)#10	2.384(2)	O(1)#1-Zn(1)-O(9)	91.24(7)
Na(3)-O(8)#1	2.439(2)	O(4)-C(1)-O(1)	121.54(18)
Na(3)-O(2)#11	2.5378(19)	O(4)-C(1)-O(2)	120.33(18)
Na(3)-O(4)#5	2.699(2)	O(1)-C(1)-O(2)	118.12(19)
Na(3)-O(9)#11	2.723(2)	O(6)-C(2)-O(7)	121.8(2)
Na(3)-O(7)#11	2.882(2)	O(6)-C(2)-O(9)	120.8(2)
Na(3)-O(8)	2.962(2)	O(7)-C(2)-O(9)	117.36(19)
Na(4)-O(4)	2.3733(19)	O(8)-C(3)-O(5)	122.6(2)
Na(4)-O(6)#12	2.4326(19)	O(8)-C(3)-O(3)	118.5(2)
Na(4)-O(7)#13	2.476(2)	O(5)-C(3)-O(3)	118.90(19)

Symmetry transformations used to generate equivalent atoms:

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

#6 x-1,y,z #7 x-1,-y+1/2,z-1/2 #8 -x+1,-y+1,-z+2 #9 x,-y+3/2,z+1/2 #10 -x+2,-y+1,-z+2

#11 -x+2,y-1/2,-z+3/2 #12 x,-y+3/2,z-1/2 #13 x-1,-y+3/2,z-1/2 #14 -x+1,y+1/2,-z+3/2

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

Table S6. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Na_4Zn(CO_3)_3$

The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2hka^* b^* U12]$

	U11	U22	U33	U23	U13	U12
Zn(1)	11(1)	14(1)	18(1)	1(1)	1(1)	0(1)
Na(1)	16(1)	18(1)	17(1)	-1(1)	1(1)	-2(1)
Na(2)	22(1)	20(1)	20(1)	-1(1)	-1(1)	-6(1)
Na(3)	35(1)	16(1)	22(1)	1(1)	2(1)	4(1)
Na(4)	17(1)	19(1)	47(1)	3(1)	3(1)	-2(1)
O(1)	11(1)	13(1)	22(1)	4(1)	3(1)	1(1)
O(2)	10(1)	18(1)	20(1)	5(1)	2(1)	1(1)
O(3)	12(1)	14(1)	25(1)	3(1)	-1(1)	2(1)
O(4)	14(1)	18(1)	27(1)	7(1)	-5(1)	2(1)
O(5)	14(1)	21(1)	28(1)	0(1)	-3(1)	0(1)
O(6)	19(1)	18(1)	23(1)	2(1)	1(1)	-6(1)
O(7)	24(1)	13(1)	30(1)	0(1)	-3(1)	-4(1)
O(8)	26(1)	14(1)	46(1)	1(1)	7(1)	-5(1)
O(9)	17(1)	42(1)	34(1)	-23(1)	6(1)	-6(1)
C(1)	11(1)	14(1)	11(1)	-2(1)	1(1)	-3(1)
C(2)	15(1)	16(1)	12(1)	-1(1)	-3(1)	-1(1)
C(3)	15(1)	13(1)	13(1)	1(1)	2(1)	0(1)

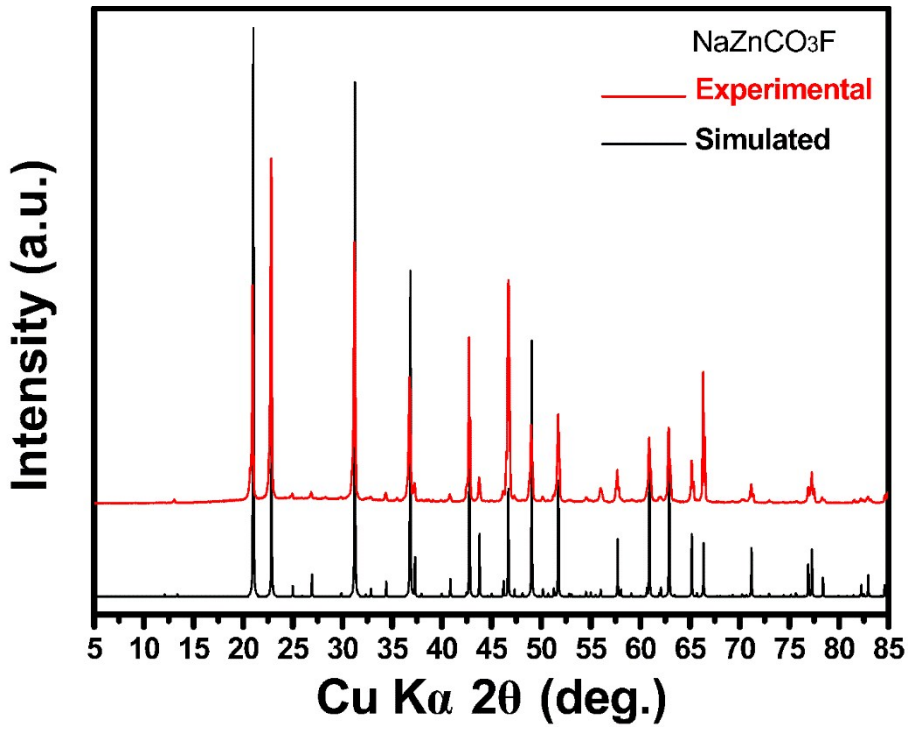

Figure S2. Simulated and experimental powder X-ray diffraction patterns of $NaZnCO_3F$

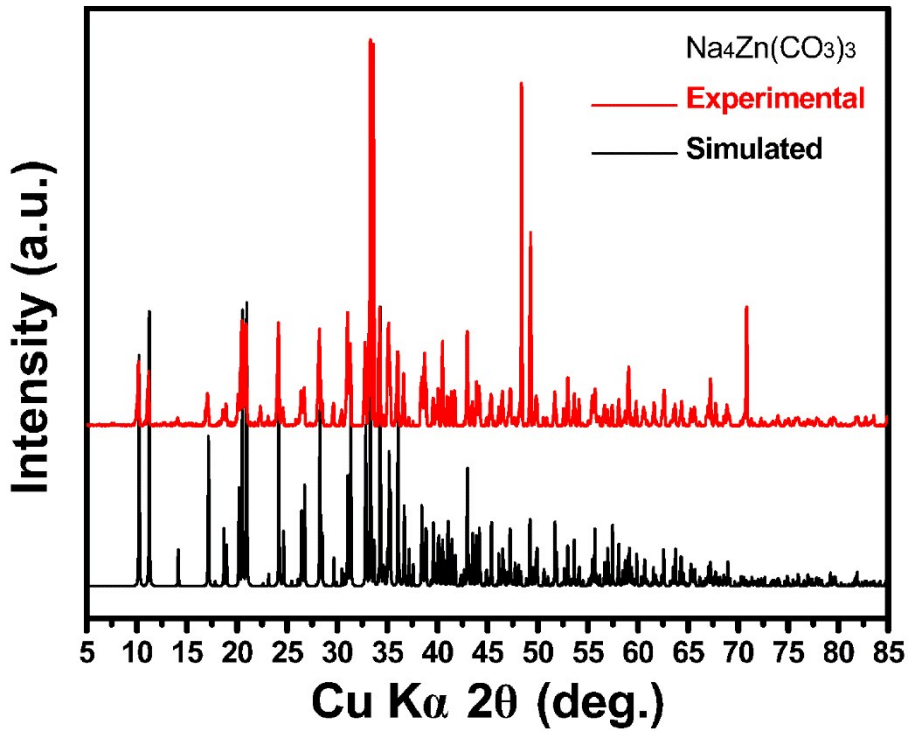

Figure S3. Simulated and experimental powder X-ray diffraction patterns of $Na_4Zn(CO_3)_3$

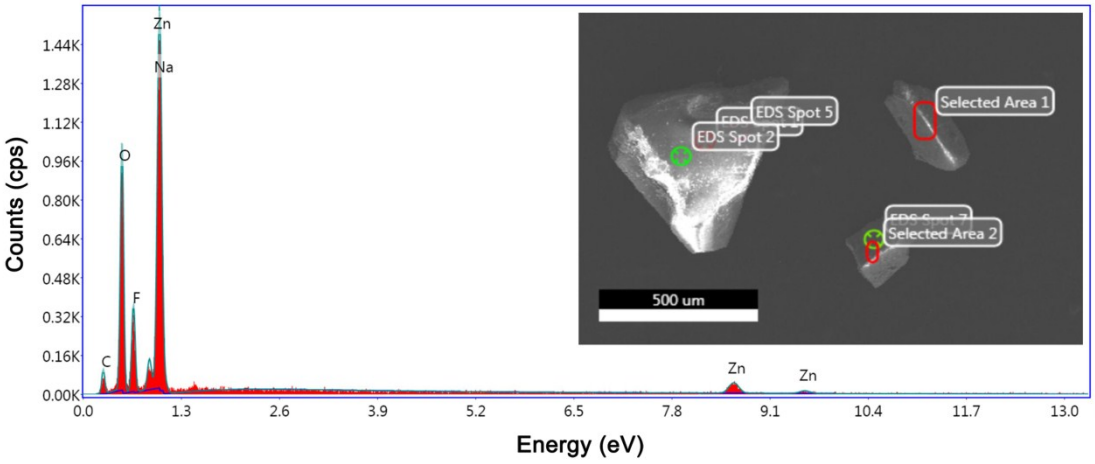

Figure S4. EDS analysis for $NaZnCO_3F$. The inset is the SEM image of the tested crystal. Scale bar, 500 μm

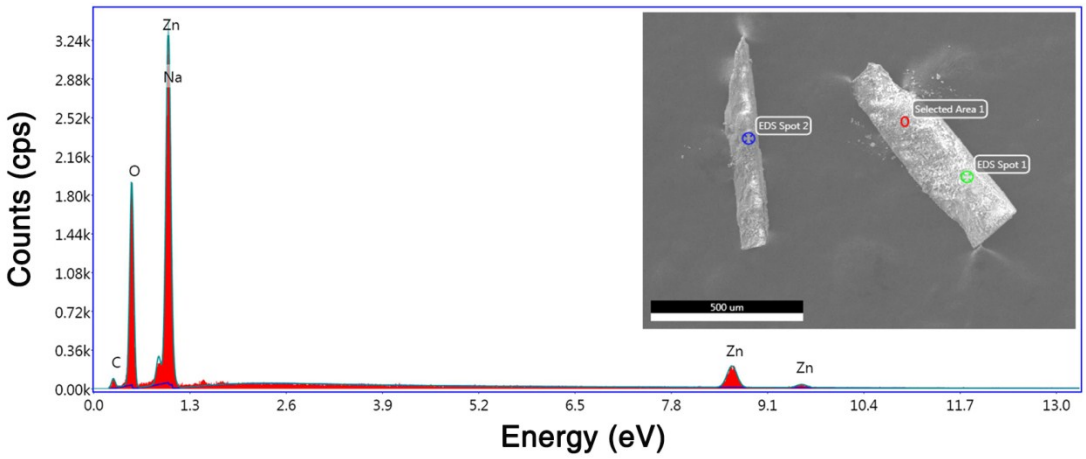

Figure S5. EDS analysis for $Na_4Zn(CO_3)_3$. The inset is the SEM image of the tested crystal. Scale bar, 500 μm

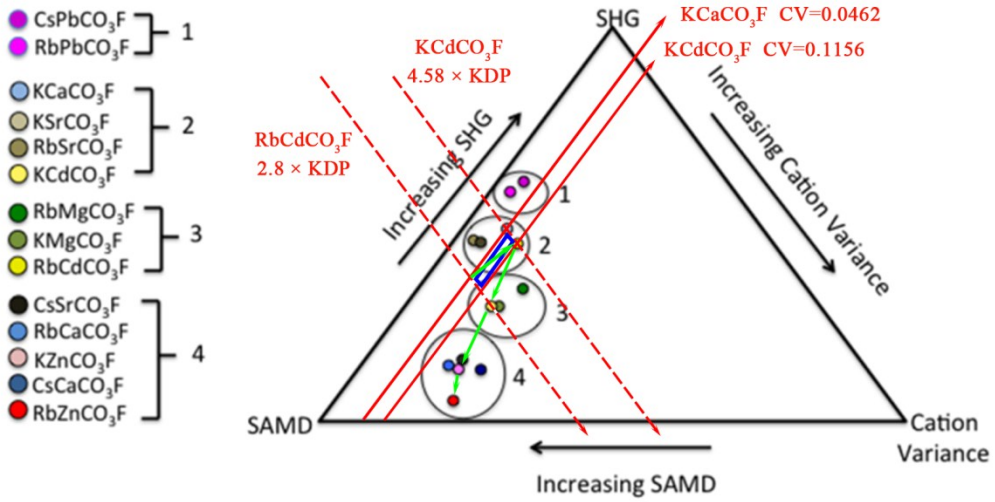

Figure S6. Relationships among SHG efficiency, SAMD, and cation variance in mixed-metal SHG active carbonate fluorides: $AMCO_3F$ (A = alkali metal, M = alkaline earth, Zn, Cd, or Pb). The position of $NaZnCO_3F$ can be located in the blue box.

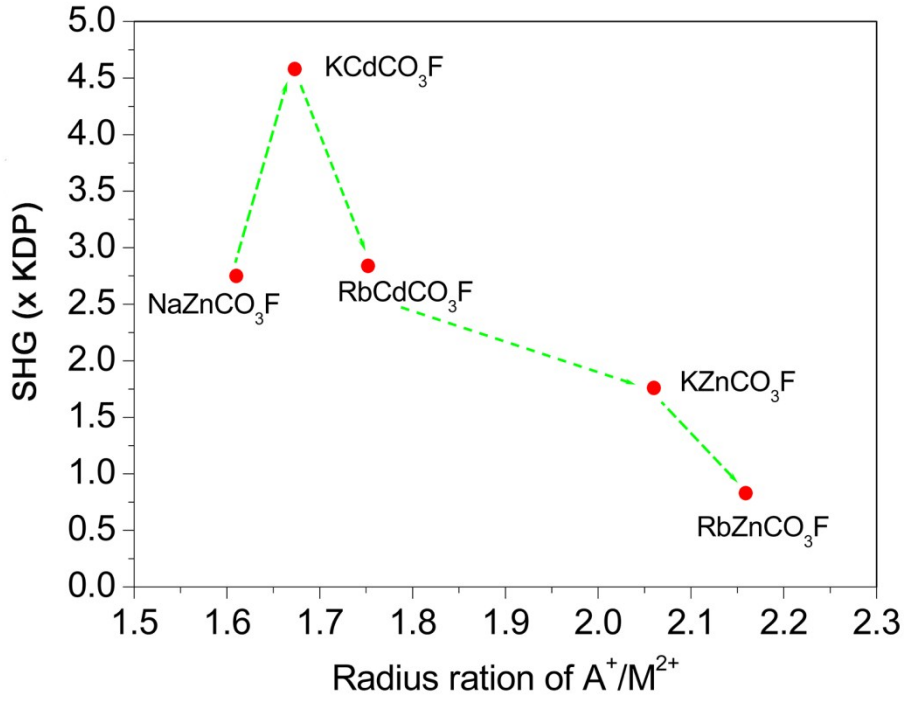

Figure S7. The relationship between SHG efficiency and radius ration of A^+/M^{2+}

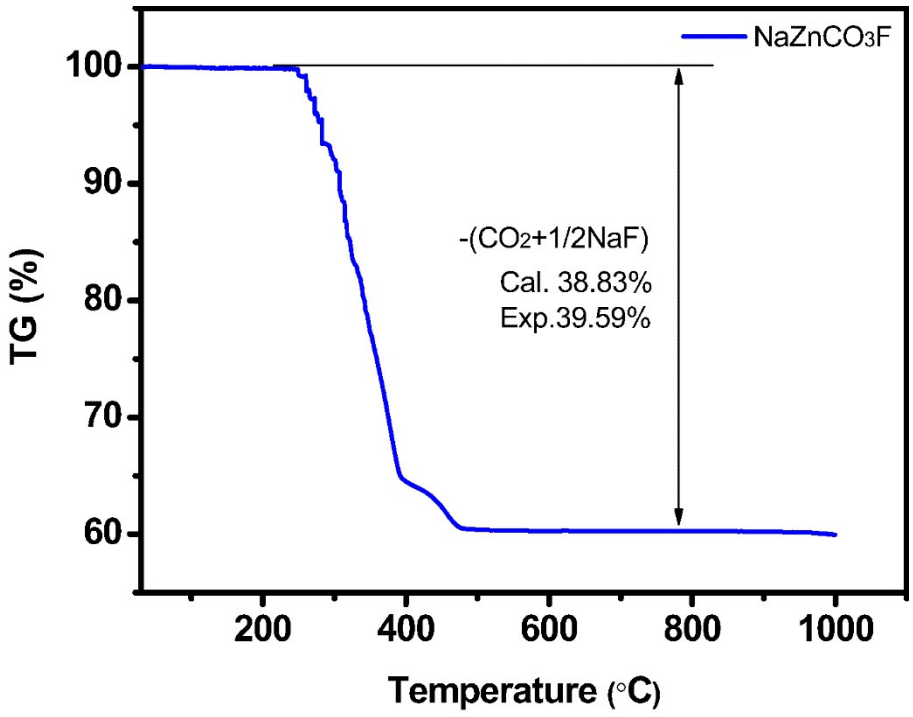

Figure S8. TG curve of $NaZnCO_3F$

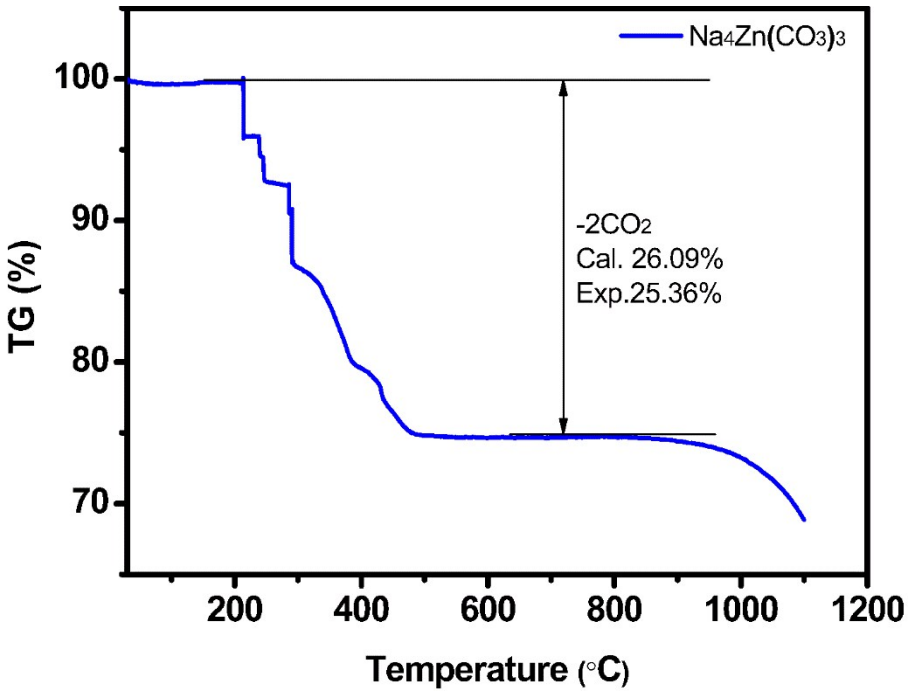

Figure S9. TG curve of $Na_4Zn(CO_3)_3$

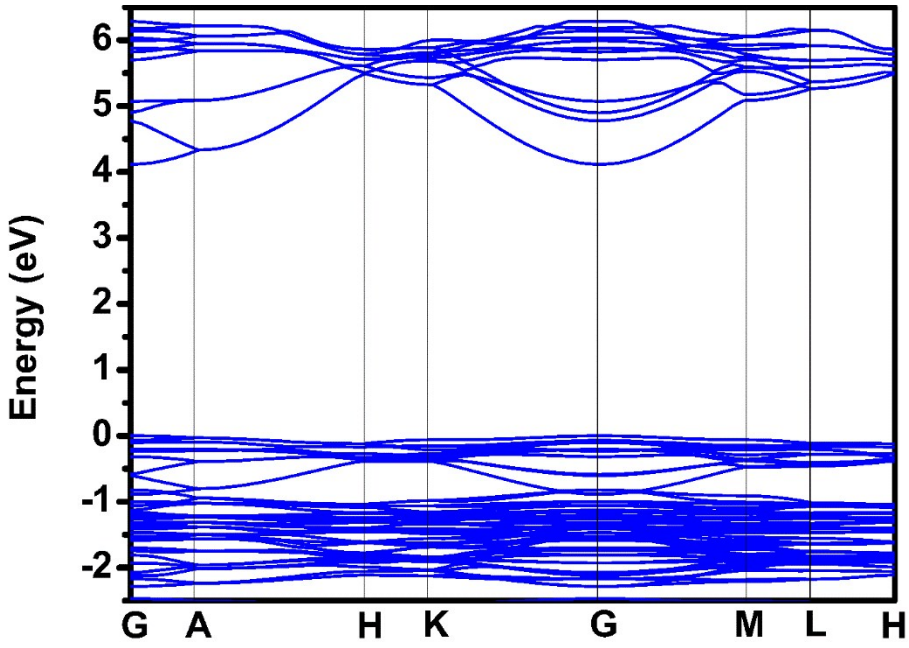

Figure S10. Calculated electronic band structure for $NaZnCO_3F$

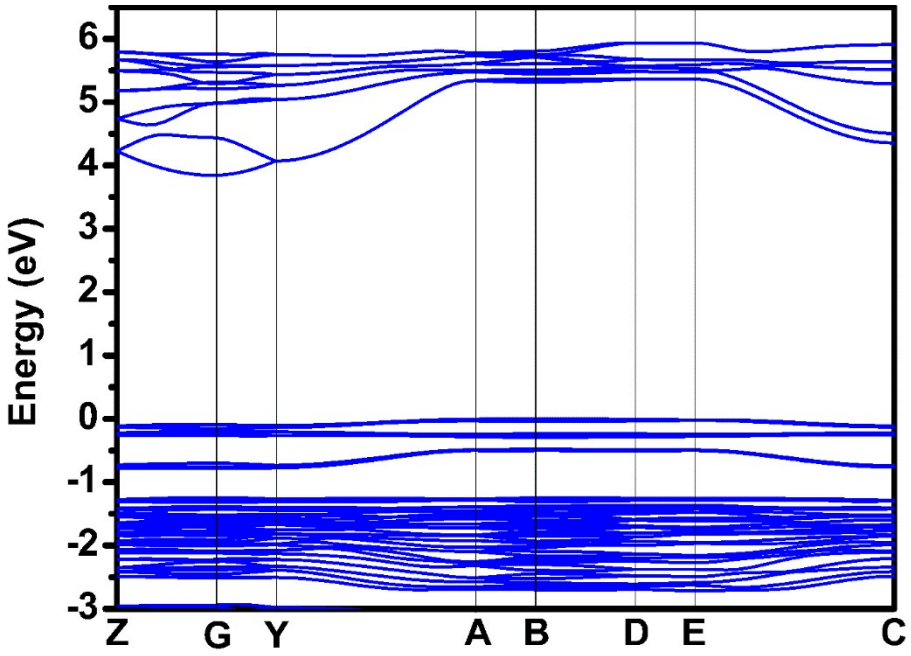

Figure S11. Calculated electronic band structure for $Na_4Zn(CO_3)_3$

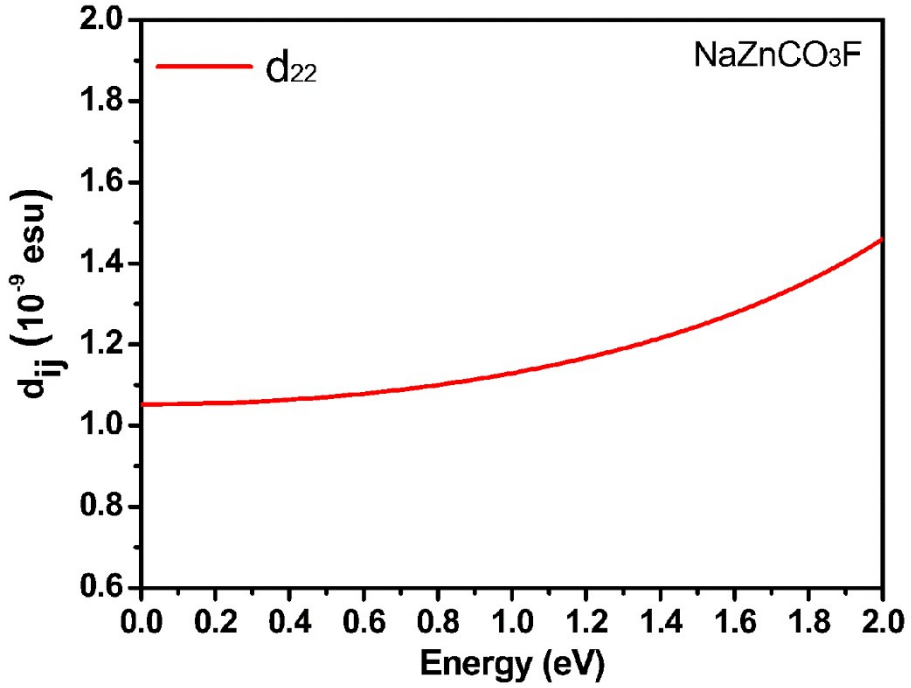

Figure 12. Calculated frequency-dependent second harmonic generation coefficient of $NaZnCO_3F$

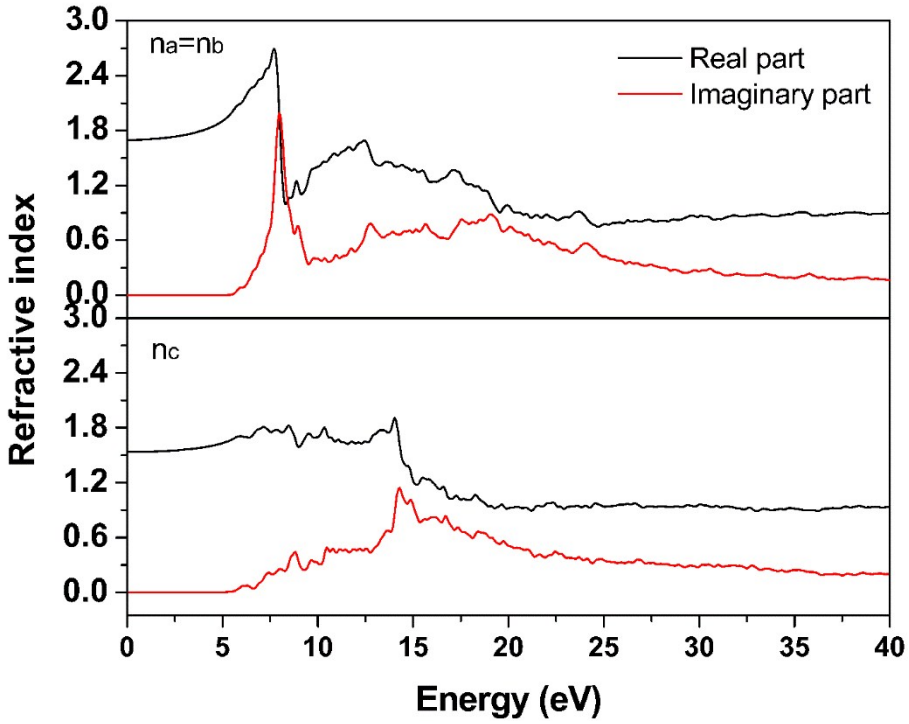

Figure S13. The calculated real part and imaginary part of the frequency-dependent refractive index for $NaZnCO_3F$

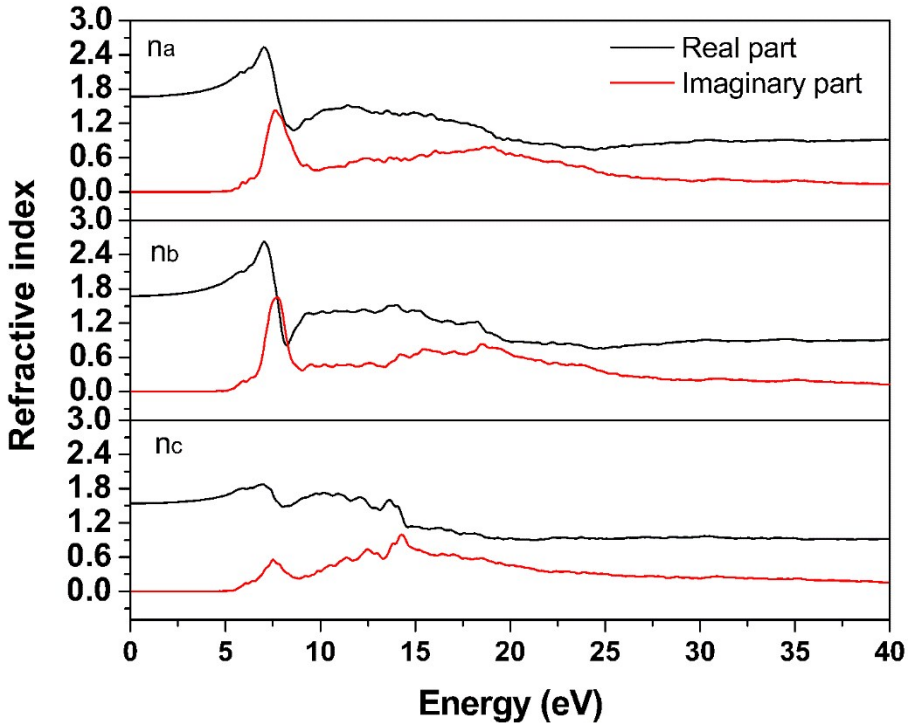

Figure S14. The calculated real part and imaginary part of the frequency-dependent refractive index for $Na_4Zn(CO_3)_3$

Reference

1 I. D. Brown, D. Altermatt, *Acta Crystallogr., Sect. B: Struct. Sci.* 1985, **41**, 244–247;
2 N. E. Brese, M. Okeeffe, *Acta Crystallogr. B* 1991, **47**, 192-197.
3 C. T. Chen, Y. C. Wu, R. K. Li, *Int. Rev. Phys. Chem.* 1989, **8**, 65-91
4 N. Ye, Q. X. Chen, B. C. Wu, C. T. Chen, *J. Appl. Phys.* 1998, **84**, 555-558.