Supplementary data

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Table S1. Atomic coordinates and equivalent isotropic displacement parameters. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	Y	z	U_{eq}(Å^2)
Yb(1)	6634(1)	-2962(1)	8402(1)	10(1)
Yb(2)	4063(1)	-4806(1)	9489(1)	8(1)
F(1)	2301(3)	-4999(2)	10442(2)	13(1)
F(2)	2402(4)	-4962(2)	8087(2)	13(1)
O(1)	6032(5)	-4972(2)	8569(3)	19(1)
O(2)	6105(4)	-4886(2)	10834(3)	14(1)
O(3)	8279(5)	-4123(2)	8738(3)	20(1)
O(4)	5108(4)	-3380(2)	9547(2)	11(1)
O(5)	4824(4)	-3583(2)	7153(2)	13(1)
O(6)	8629(5)	-5500(2)	8777(3)	19(1)
O(7)	8741(4)	-2552(2)	9899(2)	14(1)
O(8)	3459(4)	-2319(2)	9899(3)	15(1)
O(9)	12356(4)	-3561(2)	9333(3)	13(1)
O(10)	3859(4)	-2424(2)	7717(2)	13(1)
O(11)	4490(4)	-3521(2)	11954(3)	17(1)
O(12)	6848(4)	-1664(2)	9082(2)	13(1)
O(13)	8634(4)	-4289(2)	11275(3)	16(1)
O(14)	4081(4)	-2416(2)	12870(3)	19(1)
O(15)	8419(4)	-5676(2)	11313(3)	19(1)
O(16)	9507(4)	-1227(2)	9645(2)	14(1)
O(17)	2091(4)	-3229(2)	6646(2)	15(1)
O(18)	1873(4)	-2994(2)	11922(3)	21(1)
C(1)	7661(6)	-4879(3)	8695(4)	12(1)
C(2)	3541(6)	-3080(3)	7154(3)	9(1)
C(3)	8392(6)	-1799(3)	9563(3)	10(1)
C(4)	7747(6)	-4958(3)	11138(3)	8(1)
C(5)	3503(6)	-2998(3)	12223(3)	11(1)
C(6)	3592(6)	-3056(3)	9591(4)	10(1)
Na(1)	4125(4)	-5010(2)	6946(2)	10(1)
Na(2)	6701(3)	-3192(2)	11126(2)	17(1)
Na(3)	6499(3)	-3246(2)	5899(2)	17(1)
Na(4)	5338(3)	-1092(1)	10278(2)	15(1)
Na(5)	5370(2)	-982(1)	7738(1)	14(1)
Na(6)	10445(2)	-3869(1)	7752(2)	15(1)
Na(7)	10446(3)	-3791(1)	10339(2)	18(1)

Na(8)	6621(3)	-6666(1)	8504(2)	18(1)

Table S2. Bond lengths (Å) for $Na_4Yb(CO_3)_3F$

Yb(1)-O(5)	2.262(3)	O(3)-C(1)	1.300(5)
Yb(1)-O(3)	2.266(3)	O(4)-C(6)	1.333(5)
Yb(1)-O(12)	2.267(3)	O(5)-C(2)	1.304(5)
Yb(1)-O(4)	2.294(3)	O(6)-C(1)	1.248(6)
Yb(1)-O(14)#1	2.311(3)	O(7)-C(3)	1.298(5)
Yb(1)-O(10)	2.399(3)	O(8)-C(6)	1.262(5)
Yb(1)-O(7)	2.499(3)	O(9)-C(6)#4	1.273(5)
Yb(1)-O(18)#1	2.603(4)	O(9)-Yb(2)#4	2.394(3)
Yb(1)-C(3)	2.672(4)	O(10)-C(2)	1.302(5)
Yb(1)-C(2)	2.740(5)	O(11)-C(5)	1.256(6)
Yb(1)-C(5)#1	2.875(5)	O(12)-C(3)	1.304(5)
Yb(1)-Na(5)	3.386(2)	O(13)-C(4)	1.275(5)
Yb(2)-F(1)	2.145(3)	O(14)-C(5)	1.312(5)
Yb(2)-F(2)	2.151(3)	O(14)-Yb(1)#5	2.311(3)
Yb(2)-O(2)	2.236(4)	O(15)-C(4)	1.267(5)
Yb(2)-O(1)	2.239(4)	O(16)-C(3)	1.266(5)
Yb(2)-O(16)#2	2.295(3)	O(16)-Yb(2)#6	2.295(3)
Yb(2)-O(9)#3	2.394(3)	O(17)-C(2)	1.258(5)
Yb(2)-O(4)	2.418(3)	O(18)-C(5)	1.291(6)
Yb(2)-C(6)	2.821(4)	O(18)-Yb(1)#5	2.603(4)
O(1)-C(1)	1.292(6)	C(5)-Yb(1)#5	2.875(5)
O(2)-C(4)	1.306(6)	C(6)-O(9)#3	1.273(5)

Symmetry transformations used to generate equivalent atoms:

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

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

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

Table S3. The values of geometrical factor

crystals	g_{111}	g_{112}	g_{113}	g_{311}	g_{322}	g_{333}
$Na_4Yb(CO_3)_3F$	-20.7319	3.40426	-1.34299	-9.82346	3.9896	1.12835

Table S4. NLO effects of **$Na_4Yb(CO_3)_3F$**

Crystals	SHG coefficient(visible) (×KDP)	Structural criterion C	densities of the $[CO_3]$ (n/V) ($Å^{-3}$)	(n/V) ×C($Å^{-3}$)
$Na_4Yb(CO_3)_3F$	4.3	0.864	0.0137	0.0118

The Anionic Group Theory Calculation.

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

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

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]:

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

$g=\max(g_{ijk})$; (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.