Supporting Information

Equivalent cation-tuned to realize a new Ce(IV) fluoride with excellent comprehensive nonlinear optical performances

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Tables and Figures

Table S1. Selected bond lengths (Å) for $NH_4Ce_3F_{13}$.

Bond	Length/Å	Bond	Length/Å
Ce1-F1	2.237(4)	Ce2-F1[6]	2.365(3)
Ce1-F1[3]	2.237(3)	Ce2-F3[7]	2.417(4)
Ce1-F2	2.197(6)	Ce2-F[4]	2.616(4)
Ce1-F2[4]	2.301(6)	Ce2-F5	2.252(4)
Ce1-F3	2.356(6)	Ce2-F5[8]	2.307(4)
Ce1-F4	2.265(3)	Ce2-F6	2.250(3)
Ce1-F4[3]	2.265(3)	Ce2-F7	2.237(4)
Ce1-F7[2]	2.455(4)	Ce2-F8	2.317(3)
Ce1-F7[1]	2.455(4)	Ce2-F9	2.305(3)

[1]1-X,1-Y,1/2+Z; [2]+X,1-Y,1/2+Z; [3]1-X,+Y,+Z; [4]1-X,2-Y,-1/2+Z; [5]-X,+Y,+Z; [6]1-X,-1+Y,+Z; [7]1-X,1-Y,-1/2+Z; [8]+X,1-Y,-1/2+Z

Table S2. Selected bond angles (°) for $NH_4Ce_3F_{13}$.

Atom	Angle/°	Atom	Angle/°
F1^3－Ce1－F1	87.0(2)	F5－Ce2－F1^7	77.39(14)
F1－Ce1－F2^4	71.10(14)	F5^8－Ce2－F1^7	145.11(14)
F1^3－Ce1－F7^4	71.10(14)	F5－Ce2－F3^6	134.00(17)
F1－Ce1－F3	130.41(12)	F5^8－Ce2－F3^6	73.26(17)
F1^3－Ce1－F3	130.41(12)	F5－Ce2－F4	76.93(14)
F1^3－Ce1－F4	87.79(14)	F5－Ce2－F5^8	136.20(9)
F1^3－Ce1－F4^3	141.74(13)	F5^8－Ce2－F8	102.64(15)
F1－Ce1－F4^3	87.79(14)	F5－Ce2－F8	79.84(16)
F1－Ce1－F4	141.74(13)	F5－Ce2－F9	73.41(19)
F1－Ce1－F7^2	69.42(14)	F6－Ce2－F1^7	68.19(15)
F1^3－Ce1－F7^1	69.42(14)	F6－Ce2－F3^6	61.22(17)
F1－Ce1－F7^2	143.57(14)	F6－Ce2－F4	72.74(14)
F1－Ce1－F7^1	143.56(14)	F6－Ce2－F5^8	123.10(16)
F1－Ce1－F1^3	78.77(14)	F6－Ce2－F5	72.95(16)
F2－Ce1－F1	78.77(14)	F6－Ce2－F8	133.56(16)
F2－Ce1－F2^4	137.89(4)	F6－Ce2－F9	137.39(19)
F2^4－Ce1－F3	143.2(2)	F7－Ce2－F1^7	71.51(15)
F2－Ce1－F3	78.9(2)	F7－Ce2－F3^6	63.64(15)
F2－Ce1－F4^4	136.87(12)	F7－Ce2－F4	139.96(14)
F2－Ce1－F4	136.87(12)	F7－Ce2－F5	144.04(16)
F2^4－Ce1－F7^1	122.51(11)	F7－Ce2－F5^8	73.71(15)
F2－Ce1－F71	69.85(13)	F7－Ce2－F6	110.30(14)
F2^4－Ce1－F7^2	122.51(11)	F7－Ce2－F8	72.79(16)
F2－Ce1－F7^2	69.85(13)	F7－Ce2－F9	112.30(17)
F3－Ce1－F7^1	61.41(11)	F8－Ce2－F1^7	69.59(15)
F3－Ce1－F7^2	61.41(11)	F8－Ce2－F3^6	135.70(17)
F4－Ce1－F2^4	71.38(14)	F9－Ce2－F1^7	127.42(15)
F4^3－Ce1－F2^4	71.38(14)	F9－Ce2－F3^6	141.8(2)
F4^3－Ce1－F3	79.33(15)	F9－Ce2－F5^8	69.54(18)
F4－Ce1－F3	79.33(15)	F9－Ce2－F8	62.96(17)
F4－Ce1－F4^3	73.48(18)	Ce1－F1－Ce2^9	145.7(2)
F4^3－Ce1－F7^2	127.91(13)	Ce1－F1－Ce1^{10}	166.0(3)
F4－Ce1－F7^2	67.06(13)	Ce1－F1－Ce2^2	115.53(12)
F4^3－Ce1－F7^1	67.06(13)	Ce1－F1－Ce2^1	115.53(12)
F4－Ce1－F7^1	127.91(13)	Ce2^1－F1－Ce2^2	111.5(3)
F7^1－Ce1－F7^2	114.2(2)	Ce2－F1－Ce1	145.92(17)
F1^7－Ce2－F3^6	88.79(16)	Ce2－F1－Ce2^2	153.23(19)
F4－Ce2－F1^7	137.96(14)	Ce2^3－F1－Ce2	125.3(3)
F4－Ce2－F3^6	85.72(14)	Ce2－F1－Ce1^6	118.67(14)
F4－Ce2－F5^8	71.58(14)	Ce2－F1－Ce2^5	115.6(2)
F4－Ce2－F8	136.04(15)	Ce2－F1－Ce2^5	116.5(2)

F4－Ce2－F9	74.80(15)

[1]1-X,1-Y,1/2+Z; [2]+X,1-Y,1/2+Z; [3]1-X,+Y,+Z; [4]1-X,2-Y,-1/2+Z; [5]-X,+Y,+Z; [6]1-X,1-Y, -1/2+Z; [7]1-X,-1+Y,+Z; [8]+X,1-Y,-1/2+Z; [9]1-X,1+Y,+Z; [10]1-X,2-Y,1/2+Z

Table S3. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $NH_4Ce_3F_{13}$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Ce1	5000	8905.1(5)	5570.6(7)	4.77(15)
Ce2	2475.7(4)	3963.7(4)	3953.0(10)	4.58(13)
F1	6946(5)	11084(4)	5150(5)	12.5(10)
F2	5000	10326(8)	7894(7)	14.7(13)
F3	5000	6390(6)	7353(8)	10.1(11)
F4	3289(4)	6926(5)	4245(4)	11.8(8)
F5	1993(5)	4517(6)	6569(5)	11.8(8)
F6	5000	3945(6)	5192(6)	12.2(15)
F7	2396(4)	1800(6)	2048(6)	11.7(9)
F8	0	2315(7)	4311(6)	10.5(11)
F9	0	625(8)	4089(8)	11.0(12)
N1	0	8981(13)	2601(15)	23(3)

Table S4. Hydrogen atom coordinates ($Å \times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $NH_4Ce_3F_{13}$.

Atom	x	y	z	U(eq)
H1A	0	8600(200)	3560(70)	100(80)
H1B	0	8080(150)	1950(150)	170(120)
H1C	840(50)	9680(70)	2430(130)	310(130)

Table S5. The quantitative analysis result of EDS.

Compound		**Molar ratio**
1	N : Ce : F	5.85 : 17.61 : 76.54 = 1 : 3.01 : 13.08
2	N : Ce : F	5.76 : 17.13 : 77.11 = 1: 2.97 : 13.39
3	N : Ce : F	5.92 : 17.84 : 76.24 = 1: 3.01 : 12.88

Table S6. Inorganic monovalent cation Ce(IV)-based fluorides.

Compound	Space group	Coordination geometry	Symmetry	Dimension	Reference
$NH_4Ce_3F_{13}$	$Pmc2_1$	CeF_9	NCS	3D	This work
Na_2CeF_6	$P\bar{6}2m$	CeF_9	NCS	3D	1
$LiCeF_5$	$I4_1/a$	CeF_9	CS	3D	2
Cs_3CeF_7	$Fm\bar{3}m$	CeF_6	CS	3D	3
Rb_3CeF_7	$Fm\bar{3}m$	CeF_6	CS	3D	3
Na_3CeF_7	$I4/mmm$	CeF_8	CS	3D	3
$CsCeF_5$	$P2_1/c$	CeF_8	CS	3D	4
Li_4CeF_8	$Pnma$	CeF_8	CS	3D	5
$(NH_4)_7Ce_6F_{31}$	$R\bar{3}$	CeF_8	CS	3D	6
$(NH_4)_2CeF_6$	$Pbcn$	CeF_8	CS	3D	7
$(NH_4)_4CeF_8$	$C2/c$	CeF_8	CS	3D	8

Table S7. Fluorides with F_{13} in the formula.

Compound	Space group	Coordination geometry	Symmetry	Dimension	Reference
$NH_4Ce_3F_{13}$	$Pmc2_1$	CeF_9	NCS	3D	This work
KBi_4F_{13}	$I\bar{4}$	BiF_3	NCS	3D	9
$NH_4Sb_4F_{13}$	$I\bar{4}$	SbF_3	NCS	3D	10
KSb_4F_{13}	$I\bar{4}$	SbF_3	NCS	3D	11
RbU_3F_{13}	$Pmc2_1$	UF_9	NCS	3D	12
NH_4UF_{13}	$Pmc2_1$	UF_9	NCS	3D	13
$RbTh_3F_{13}$	$Pmc2_1$	ThF_9	NCS	3D	14
$[(C_5H_6N_2)_2H](Sb_4F_{13})$	$P1$	SbF_4, SbF_5	NCS	3D	15

Table S8. The bandgaps, SHG efficiency and LIDTs of reported inorganic metal fluorides.

Compound	Space group	SHG efficiency (× KDP)	LIDT (× AGS)	Band gap(eV)	Reference
$BaMgF_4$	$Cmc2_1$	0.085	---	9.28	16
$BaZnF_4$	$Cmc2_1$	0.16	---	7.27	16
Na_2SbF_5	$P2_12_12_1$	0.17	---	5.0	17
$CsNaTaF_7$	$Cmc2_1$	0.2	---	5.14	18
Li_2CaHfF_8	$I\bar{4}$	0.3	---	---	19
Li_2CaZrF_8	$I\bar{4}$	0.36	---	---	19
KNa_2ZrF_7	$Pmn2_1$	0.4	50	5.07	20
$K_3Ba_2Zr_6F_{31}$	$P6_3mc$	0.5	---	---	21
KBi_4F_{13}	$I\bar{4}$	0.5	23.1	4.24	10
$K_2BaHf_2F_{12}$	$Imm2$	0.36	---	---	22
$K_2BaZr_2F_{12}$	$Imm2$	0.6	---	---	22
$NH_4Ce_3F_{13}$	$Pmc2_1$	1.2	39	4.26	This work
Na_2CeF_6	$P\bar{6}2m$	2.1	over 20	3.89	1
$NaSb_3F_{10}$	$P6_3$	3.2	1.3 GM cm^{-2}	5.0	23
SbF_3	$Ama2$	5.8	---	4.3	24

Table S9. The distortion degrees of the Ce-centered polyhedra in $NH_4Ce_3F_{13}$.

compound	**polyhedron**	**Δd[a]**
$NH_4Ce_3F_{13}$	$Ce(1)F_9$	1.52E-03
	$Ce(2)F_9$	5.97E-04

[a] $\Delta d = \frac{1}{C}\sum[(d_n - d)/d]^2$ (d_n is the single bond length, d is the average bond length, and C is the coordination number.)

Table S10. Calculated dipole moment results of $NH_4Ce_3F_{13}$.

NO.	**Unit**	**Dipole moment**			
		x (esu cm)	**y (esu cm)**	**z (esu cm)**	**Magnitude Debye**
1	$Ce(1)F_9$	-0.0001	0.8088	0.7481	1.1017
2	$Ce(1)F_9$	-0.0001	-0.8087	0.7483	1.1019
3	$Ce(2)F_9$	-0.4771	0.1648	0.2262	0.5531
4	$Ce(2)F_9$	0.4770	0.1650	0.2264	0.5532
5	$Ce(2)F_9$	-0.4777	-0.1641	0.2259	0.5533
6	$Ce(2)F_9$	0.4777	-0.1640	0.2261	0.5533
Unit cell		2.2716	-0.0004	0.0017	2.4009

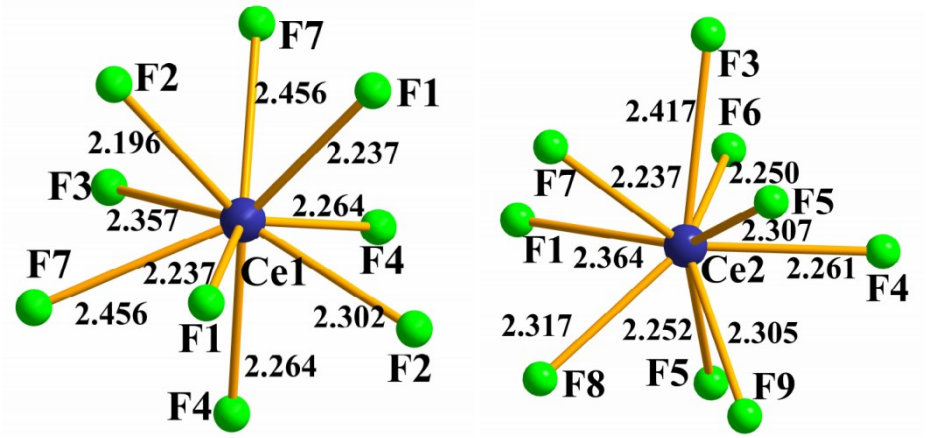

Figure S1. The coordination environment of Ce(1) and Ce(2) atoms in $NH_4Ce_3F_{13}$.

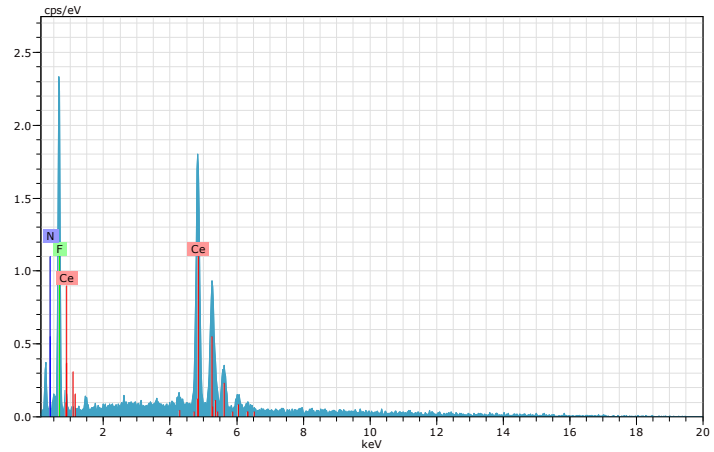

Figure S2. The EDS image for single-crystals of $NH_4Ce_3F_{13}$.

Figure S3. The arrangement of 1*D* $\{[CeF_6]^{2-}\}_\infty$ chains and the whole structure of Na_2CeF_6.

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