A Deep-Ultraviolet Nonlinear-Optical Material with Wide Band Gap and Large Static Dielectric Polarizability Coefficient: $Na_6Si_3F_{18}$

Changcheng Tang*[1,2], Xingxing Jiang[3,4], Xiuyu Wu[1,2], Yuechen Gong[1,2], Chao Yang[1,2], Ruixin Guo[5,6], Panpan Wang[1,2], Yongming Huang[1,2], Dakun Zhou[1,2], Huaiming Chen[1,2], Zheshuai Lin[3,4]

Content

1. Tables

Table S1. Crystallographic record and structural refinement information

Empirical formula	$Na_6Si_3F_{18}$
Formula weight(g/mol)	564.17
Temperature(K)	150(2)
Wavelength (Å)	0.71073
Crystal system	*Trigonal*
Space group	*P321*
a(Å)	8.8384(2)
b(Å)	8.8384(2)
c(Å)	5.0117(2)
α(°)	90
β(°)	90
γ(°)	120
Volume(Å ^{3})	339.05(2)
Z	3
Density (g cm^{-3})	2.763
μ (mm^{-1})	0.753
F(000)	270
R1,wR2 [I>2σ(I)][a]	0.0213, 0.0489
R1,wR2[all data][a]	0.0213, 0.0489

[a] $R_1 = \sum \big| \, |F_o| - |F_c| \, \big| / \sum |F_o|$;.w$R_2 = \{(\sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4\}^{1/2}$

Table S2. Fractional atomic coordinates and isotropic or equivalent isotropic

Atom	***Wyck.***	***x/a***	***y/b***	***z/c***	U_{eq}	***BVS***
Si1	2d	1/3	2/3	0.9943(2)	0.0094(2)	4.48
Si2	6g	0	1	1/2	0.0082(3)	4.60
Na1	3e	0	0.71224(13)	1	0.0131(3)	1.24
Na2	3f	0	0.37756(15)	1/2	0.0135(3)	0.99
F1	6g	0.15483(15)	0.5972(2)	0.7993(3)	0.0139(3)	1.12
F2	6g	0.2606(2)	0.7731(2)	1.1882(4)	0.0149(3)	1.10
F3	6g	0.0949(3)	0.9151(3)	0.6913(3)	0.0181(3)	1.15

Table S3. Atomic displacement parameters (Å^2) for $Na_6Si_3F_{18}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1	0.0092(3)	0.0092(3)	0.0098(5)	0.000	0.000	0.00458(15)
Si2	0.0073(4)	0.0073(4)	0.0101(7)	0.000	0.000	0.00365(18)
Na1	0.0151(6)	0.0125(4)	0.0127(7)	0.0025(5)	0.0049(9)	0.0075(3)
Na2	0.0176(7)	0.0137(4)	0.0106(6)	−0.0005(5)	−0.0010(9)	0.0088(3)
F1	0.0090(6)	0.0162(7)	0.0167(6)	−0.0050(7)	−0.0027(6)	0.0064(6)
F2	0.0152(8)	0.0152(8)	0.0166(6)	−0.0053(8)	−0.0029(8)	0.0093(6)
F3	0.0181(8)	0.0208(7)	0.0182(7)	0.0091(10)	0.0014(10)	0.0119(6)

Table S4. Selected geometric information (Å, º), Bond lengths and angles for $Na_6Si_3F_{18}$

Si1–F2	1.6877(17)	F2–Si1–F1	90.61(8)	F3–Na1–F2	99.77(8)
Si1–F2$^{\#1}$	1.6877(17)	F2–Si1–F1	89.36(8)	F3–Na1–F2	99.55(8)
Si1–F2$^{\#2}$	1.6877(17)	F1–Si1–F1	89.88(7)	F2–Na1–F2	148.93(10)
Si1–F1$^{\#1}$	1.6888(13)	F2–Si1–F1	179.10(9)	F3–Na1–F1	89.09(6)
Si1–F1$^{\#2}$	1.6888(13)	F2–Si1–F1	90.61(8)	F2–Na1–F1	94.04(7)
Si1–F1	1.6888(13)	F1–Si1–F1	89.88(7)	F2–Na1–F1	62.23(5)
Si2–F3	1.6780(14)	F3–Si2–F3	91.60(14)	F1–Na1–F1	84.82(9)
Si2–F3$^{\#4}$	1.6780(14)	F3–Si2–F3	90.59(8)	F1–Na2–F1	113.37(9)
Si2–F3$^{\#5}$	1.6780(14)	F3–Si2–F3	176.96(15)	F1–Na2–F2	87.35(5)
Si2–F3$^{\#6}$	1.6780(14)	F3–Si2–F3	90.60(8)	F1–Na2–F2	93.50(5)
Si2–F3$^{\#7}$	1.6780(14)	F3–Si2–F3	87.29(13)	F3–Na1–F1	160.18(6)
Si2–F3$^{\#8}$	1.6780(14)	F3–Si2–F3	87.29(13)	F2–Na2–F2	178.46(10)
F1–Na2	2.2879(14)	F3–Si2–F3	91.60(14)	F1–Na2–F3	151.80(6)
F1–Na1	2.3045(17)	F3–Si2–F3	87.29(13)	F1–Na2–F3	94.76(5)
F2–Na1	2.2900(16)	F3–Si2–F3	176.96(15)	F2–Na2–F3	93.08(8)
F2–Na2$^{\#3}$	2.3363(17)	F3–Na1–F3	102.43(9)	F2–Na2–F3	85.57(7)
F2–Si1–F2	90.16(9)	F3–Na1–F2	99.54(8)	F3–Na2–F3	57.23(8)

Symmetry transformations used to generate equivalent atoms:
#1: -X+Y, 1-X, +Z; #2: 1-Y, 1+X-Y, +Z; #3: -X+Y, 1-X, 1+Z; #4: -X, -X+Y, 1-Z; #5: 1-Y, 2+X-Y, +Z; #6: -1+Y, 1+X, 1-Z; #7: -1-X+Y, 1-X, +Z; #8: 1+X-Y, 2-Y, 1-Z; #9: -Y, 1+X-Y, +Z; #10: +X, 1+Y, +Z; #11: -X, -X+Y, 2-Z; #12: -1+Y, +X, 2-Z; #13: +X, +Y, 1+Z; #14: 1-Y, 1+X-Y, -1+Z; #15: -1+Y, +X, 1-Z; #16: +X, -1+Y, +Z; #17: +X, +Y, -1+Z; #18: -1-X+Y, -X, -1+Z; #19: -1-X+Y, -X, +Z;

Table S5. Torsion angles for $Na_6Si_3F_{18}$

F2–Si1–F1–Na2	−158.92(12)	$F2^{\#1}$–Si1–F2–$Na2^{\#3}$	108.78(7)
$F2^{\#1}$–Si1–F1–Na2	−68.77(13)	$F1^{\#2}$–Si1–F2–$Na2^{\#3}$	−70.75(15)
$F1^{\#2}$–Si1–F1–Na2	110.47(6)	F1–Si1–F2–$Na2^{\#3}$	−160.62(14)
$F1^{\#1}$–Si1–F1–Na2	20.59(13)	Na1–Si1–F2–$Na2^{\#3}$	−161.7(2)
Na1–Si1–F1–Na2	−157.88(16)	$Na1^{\#2}$–Si1–F2–$Na2^{\#3}$	−25.81(14)
$Na1^{\#2}$–Si1–F1–Na2	111.99(11)	$Na1^{\#1}$–Si1–F2–$Na2^{\#3}$	108.50(13)
$Na1^{\#1}$–Si1–F1–Na2	−24.34(11)	$F3^{\#4}$–Si2–F3–Na1	−74.10(15)
F2–Si1–F1–Na1	−1.04(9)	$F3^{\#5}$–Si2–F3–Na1	103.81(7)
$F2^{\#1}$–Si1–F1–Na1	89.12(8)	$F3^{\#6}$–Si2–F3–Na1	13.20(14)
$F1^{\#2}$–Si1–F1–Na1	−91.64(11)	$F3^{\#7}$–Si2–F3–Na1	−164.6(2)
$F1^{\#1}$–Si1–F1–Na1	178.48(9)	$Na2^{\#8}$–Si2–F3–Na1	−30.44(13)
$Na1^{\#2}$–Si1–F1–Na1	−90.13(7)	$Na2^{\#2}$–Si2–F3–Na1	−164.6(2)
$Na1^{\#1}$–Si1–F1–Na1	133.55(6)	$Na2^{\#9}$–Si2–F3–Na1	105.90(15)
$F2^{\#2}$–Si1–F2–Na1	−179.72(9)	$F3^{\#4}$–Si2–F3–$Na2^{\#2}$	90.52(8)
$F2^{\#1}$–Si1–F2–Na1	−89.56(13)	$F3^{\#5}$–Si2–F3–$Na2^{\#2}$	−91.58(15)
$F1^{\#2}$–Si1–F2–Na1	90.92(8)	$F3^{\#6}$–Si2–F3–$Na2^{\#2}$	177.82(11)
F1–Si1–F2–Na1	1.05(9)	$F3^{\#7}$–Si2–F3–$Na2^{\#2}$	−0.001(0)
$Na1^{\#2}$–Si1–F2–Na1	135.86(7)	$Na2^{\#8}$–Si2–F3–$Na2^{\#2}$	134.18(7)
$Na1^{\#1}$–Si1–F2–Na1	−89.83(9)	$Na2^{\#9}$–Si2–F3–$Na2^{\#2}$	−89.48(8)
$F2^{\#2}$–Si1–F2–$Na2^{\#3}$	18.62(16)		

Symmetry transformations used to generate equivalent atoms:
#1: 1-Y, 1+X-Y, +Z; #2: -X+Y, 1-X, +Z; #3: -X+Y, 1-X, 1+Z; #4: -X, -X+Y, 1-Z;
#5: 1-Y, 2+X-Y, +Z; #6: -1-X+Y, 1-X, +Z; #7: 1+X-Y, 2-Y, 1-Z; #8: -Y, 1+X-Y, +Z;
#9: +X, 1+Y, +Z;

Table S6. The calculated refractive indices n and the birefringence Δn of $Na_6Si_3F_{18}$ crystal

Wavelength(nm)	$n_{(100)}$	$n_{(010)}$	$n_{(001)}$	Δn
5533.64958	1.09341	1.09341	1.08951	0.0039
4773.57971	1.09342	1.09342	1.08951	0.00391
4197.07744	1.09342	1.09342	1.08952	0.0039
3744.81807	1.09343	1.09343	1.08953	0.0039
3380.54482	1.09344	1.09344	1.08953	0.00391
3080.85762	1.0934 5	1.09345	1.08954	0.00391
2829.98491	1.09346	1.09346	1.08955	0.00391
2433.63448	1.09348	1.09348	1.08958	0.0039
2011.13705	1.09352	1.09352	1.08962	0.0039
1559.81046	1.09361	1.09361	1.0897	0.00391
1076.60207	1.09384	1.09384	1.08993	0.00391
1044.25235	1.09387	1.09387	1.08996	0.00391
985.05533	1.09393	1.09393	1.09001	0.00392
907.85679	1.09403	1.09403	1.09011	0.00392
862.78017	1.0941	1.0941	1.09017	0.00393
821.96754	1.09417	1.09417	1.09024	0.00393
802.9757	1.09421	1.09421	1.09028	0.00393
784.84217	1.09424	1.09425	1.09032	0.00392
750.92506	1.09432	1.09432	1.09039	0.00393
705.2117	1.09445	1.09445	1.09052	0.00393
691.18601	1.09449	1.09449	1.09056	0.00393
652.26821	1.09463	1.09463	1.09069	0.00394
606.71873	1.09483	1.09483	1.09088	0.00395
558.01	1.0951	1.0951	1.09114	0.00396
532.36636	1.09527	1.09527	1.09131	0.00396
501.62943	1.09551	1.09551	1.09155	0.00396
455.59658	1.09597	1.09598	1.092	0.00397
407.51536	1.09665	1.09665	1.09265	0.004
357.2464	1.09768	1.09768	1.09366	0.00402
304.10351	1.09944	1.09944	1.09537	0.00407
266.75588	1.10144	1.10144	1.09732	0.00412
212.8428	1.10686	1.10687	1.10261	0.00425
192.77224	1.11051	1.11051	1.10617	0.00434
177.05822	1.11463	1.11463	1.1102	0.00443
161.43158	1.12064	1.12064	1.1161	0.00454
148.97546	1.12787	1.12787	1.12321	0.00466
140.54108	1.13498	1.13498	1.13024	0.00474
133.01056	1.14411	1.14411	1.13931	0.0048
124.88501	1.1602	1.1602	1.1555	0.0047
120.13621	1.17571	1.17571	1.17144	0.00427
118.09502	1.18425	1.18425	1.18027	0.00398

Table S7. The calculated dielectric polarizabilities matrix of $Na_6Si_3F_{18}$ crystal compared with α-SiO_2 and *Pmn2₁* phase SrB_4O_7

crystal	phase	Optical (f->infinity)	Static (f=0)
SiO_2	*P3₁21*	$\begin{bmatrix} 13.56004 & 0 & 0 \\ 0 & 13.56004 & 0 \\ 0 & 0 & 13.79581 \end{bmatrix}$	$\begin{bmatrix} 33.76732 & 0 & 0 \\ 0 & 33.76732 & 0 \\ 0 & 0 & 35.34961 \end{bmatrix}$
$Na_6Si_3F_{18}$	*P321*	$\begin{bmatrix} 21.55810 & 0 & 0 \\ 0 & 21.55810 & 0 \\ 0 & 0 & 21.17250 \end{bmatrix}$	$\begin{bmatrix} 100.00777 & 0 & 0 \\ 0 & 100.00777 & 0 \\ 0 & 0 & 152.20484 \end{bmatrix}$
SrB_4O_7	*Pmn2₁*	$\begin{bmatrix} 34.77742 & 0 & 0 \\ 0 & 34.49517 & 0 \\ 0 & 0 & 34.66299 \end{bmatrix}$	$\begin{bmatrix} 130.732770 & 0 & 0 \\ 0 & 155.57194 & 0 \\ 0 & 0 & 144.6656 \end{bmatrix}$

Table S8. The SHG tensors of $Na_6Si_3F_{18}$ compared with SiO_2 and SrB_4O_7 .

crystal	phase	SHG tensors (pm/v)
SiO_2	*$P3_121$*	d_{112}=-0.50 d_{222}=0.50
$Na_6Si_3F_{18}$	*P321*	d_{112}=0.78×10^{-3} d_{222}=-0.78×10^{-3}
SrB_4O_7	*$Pmn2_1$*	d_{113}=1.17 d_{223}=0.67 d_{333}=-1.97

2. Figures

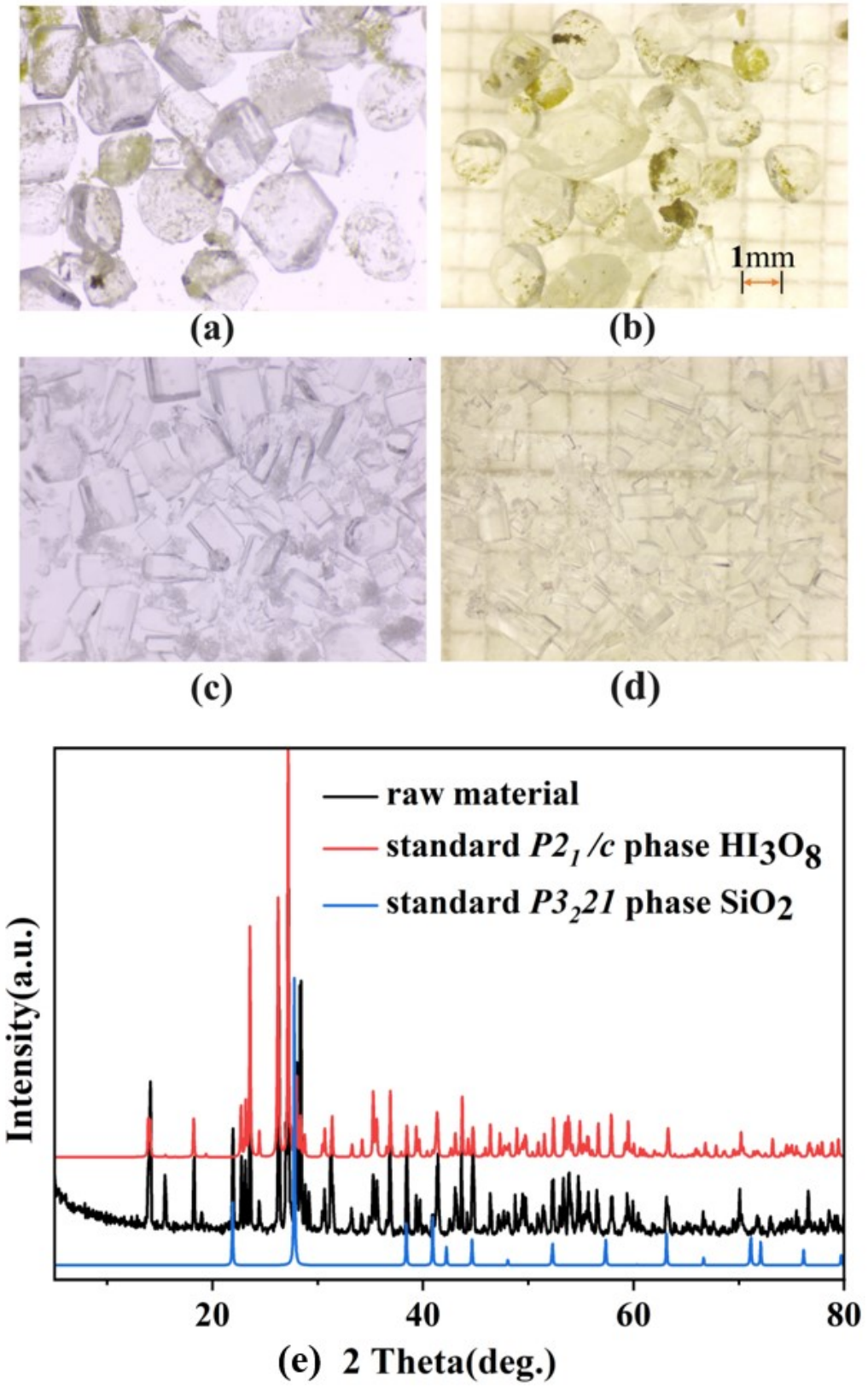

Figure S1. As-grown crystals of $Na_6Si_3F_{18}$ and compared raw material XRD. (a) and (b) Impurity crystallization sample; (c) and (d) Sel-crystallization sample;(e) the compared XRD of raw material (HIO_3) with $P2_1/c$ phase HI_3O_8 and $P3_221$ phase SiO_2.

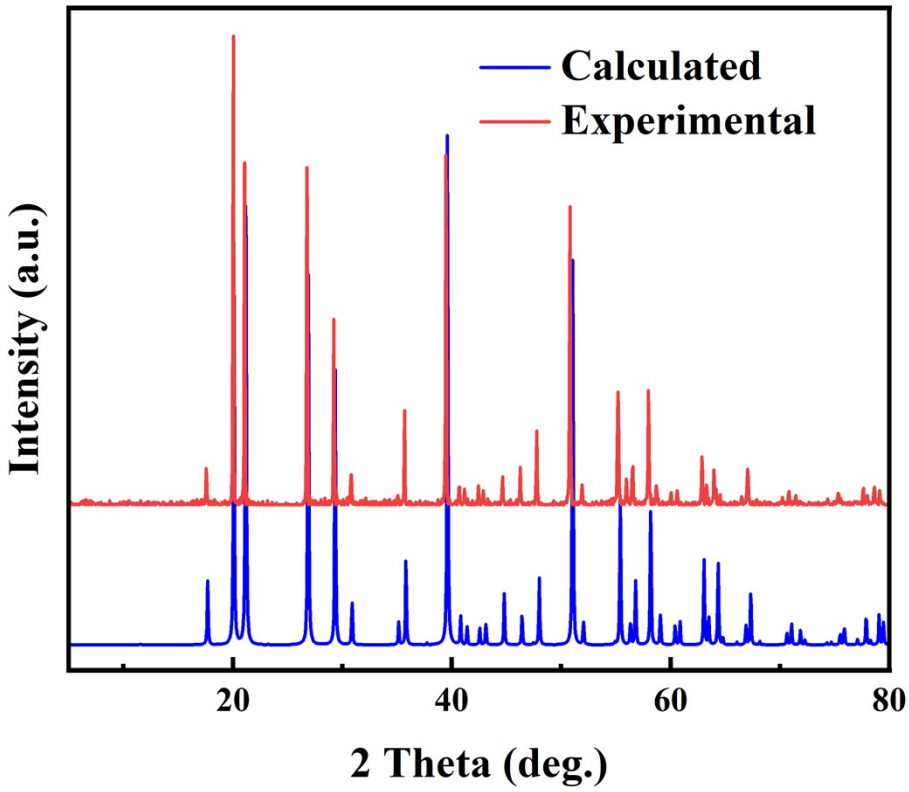

Figure S2. Calculated(blue) and experimental(red) powder XRD patterns of $Na_6Si_3F_{18}$.

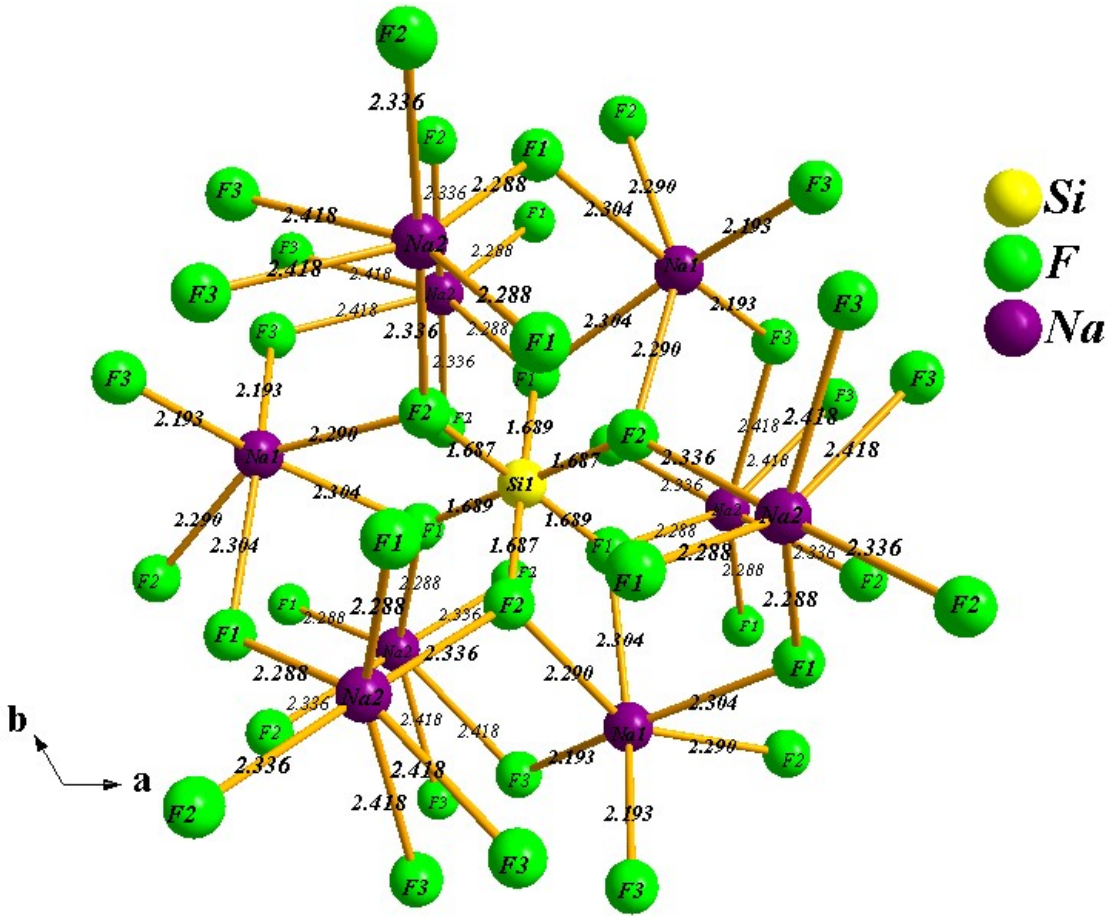

Figure S3. The [$Si1Na_9F_{42}$] group viewed down [0 0 1].

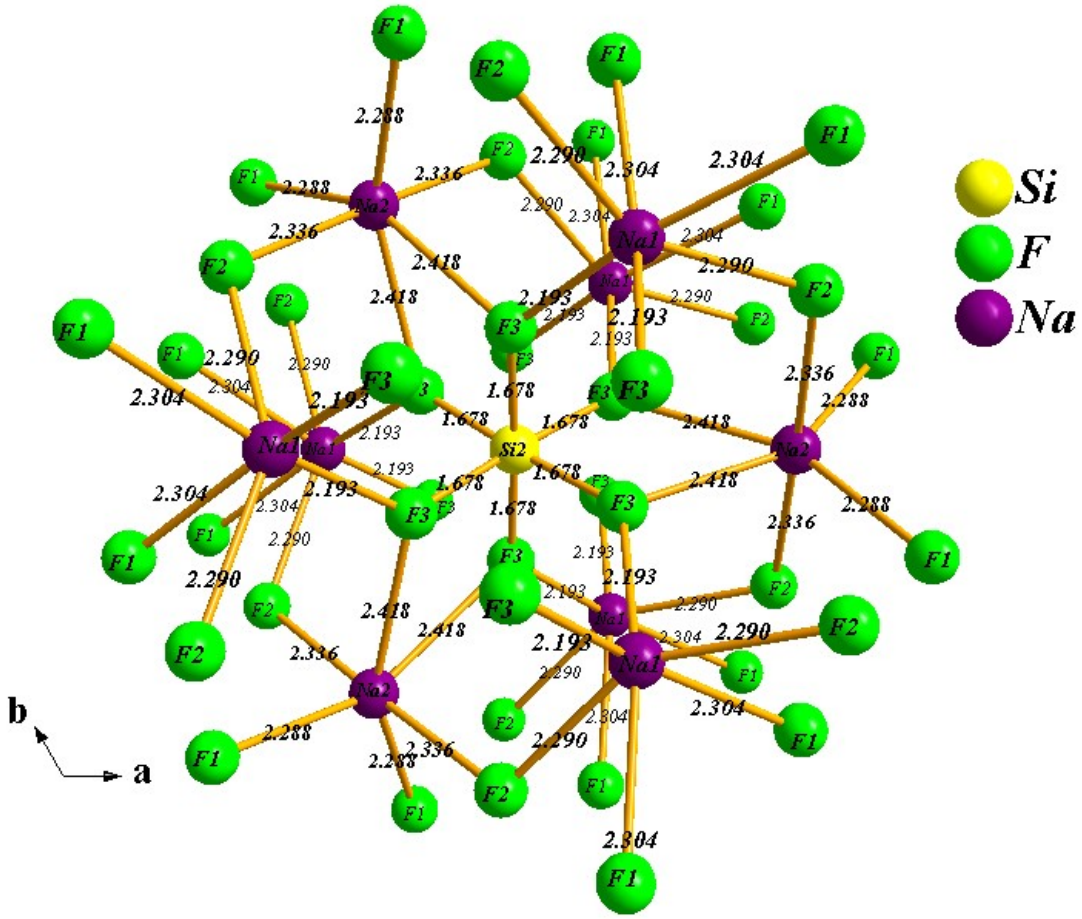

Figure S4. The [$Si2Na_9F_{42}$] group viewed down [0 0 1].

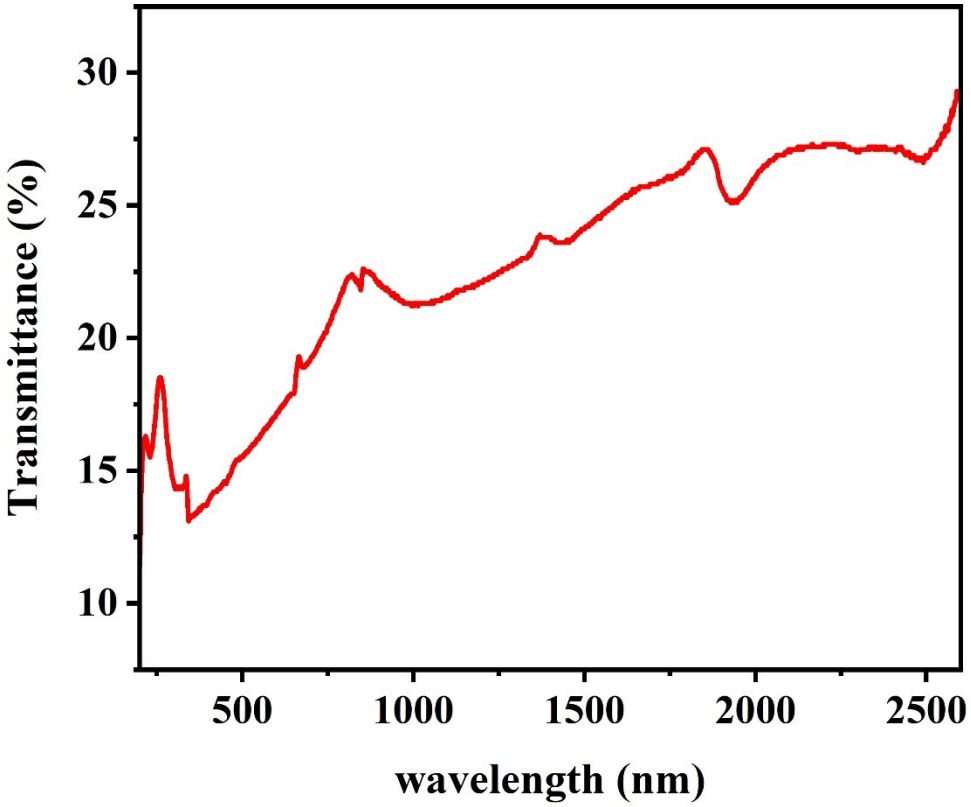

Figure S5. The UV-vis-NIR transmittance spectra of $Na_6Si_3F_{18}$.

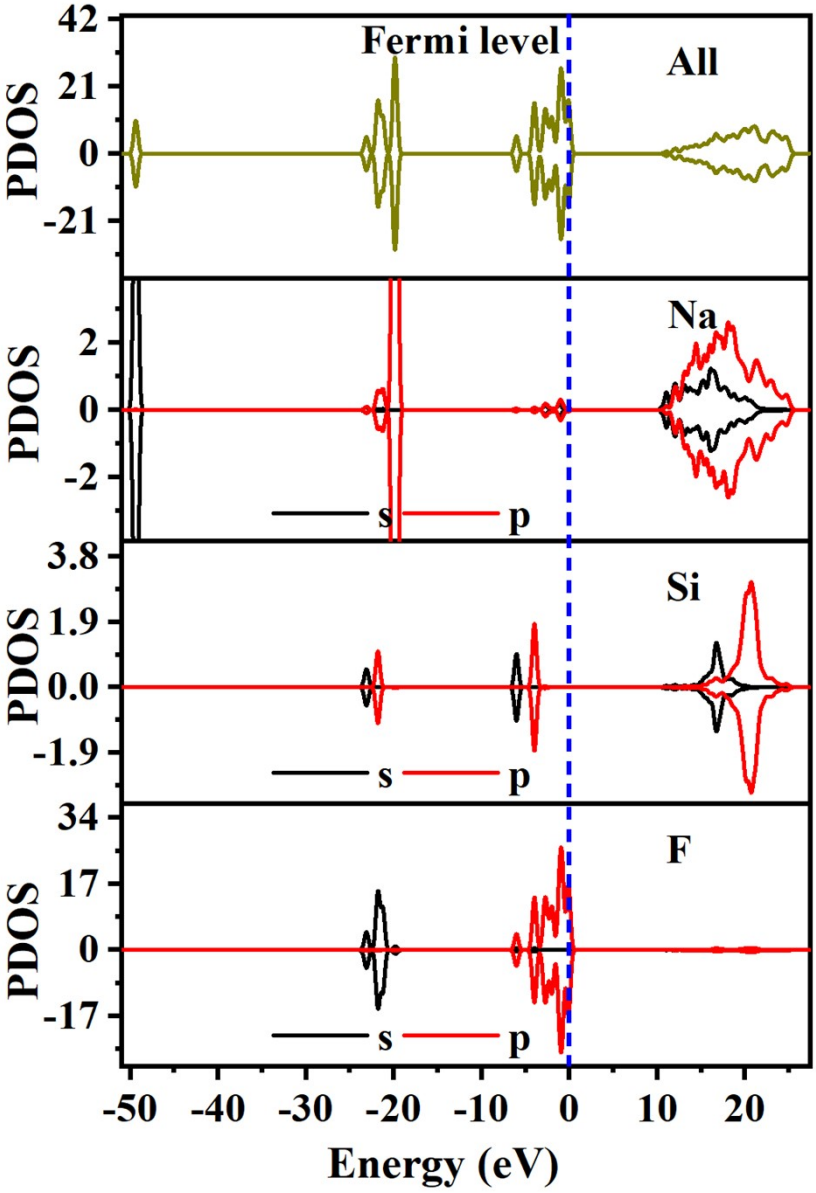

Figure S6. The Na and Si compared partial density of state with spin polarized projected on the constituent elements of $Na_6Si_3F_{18}$.

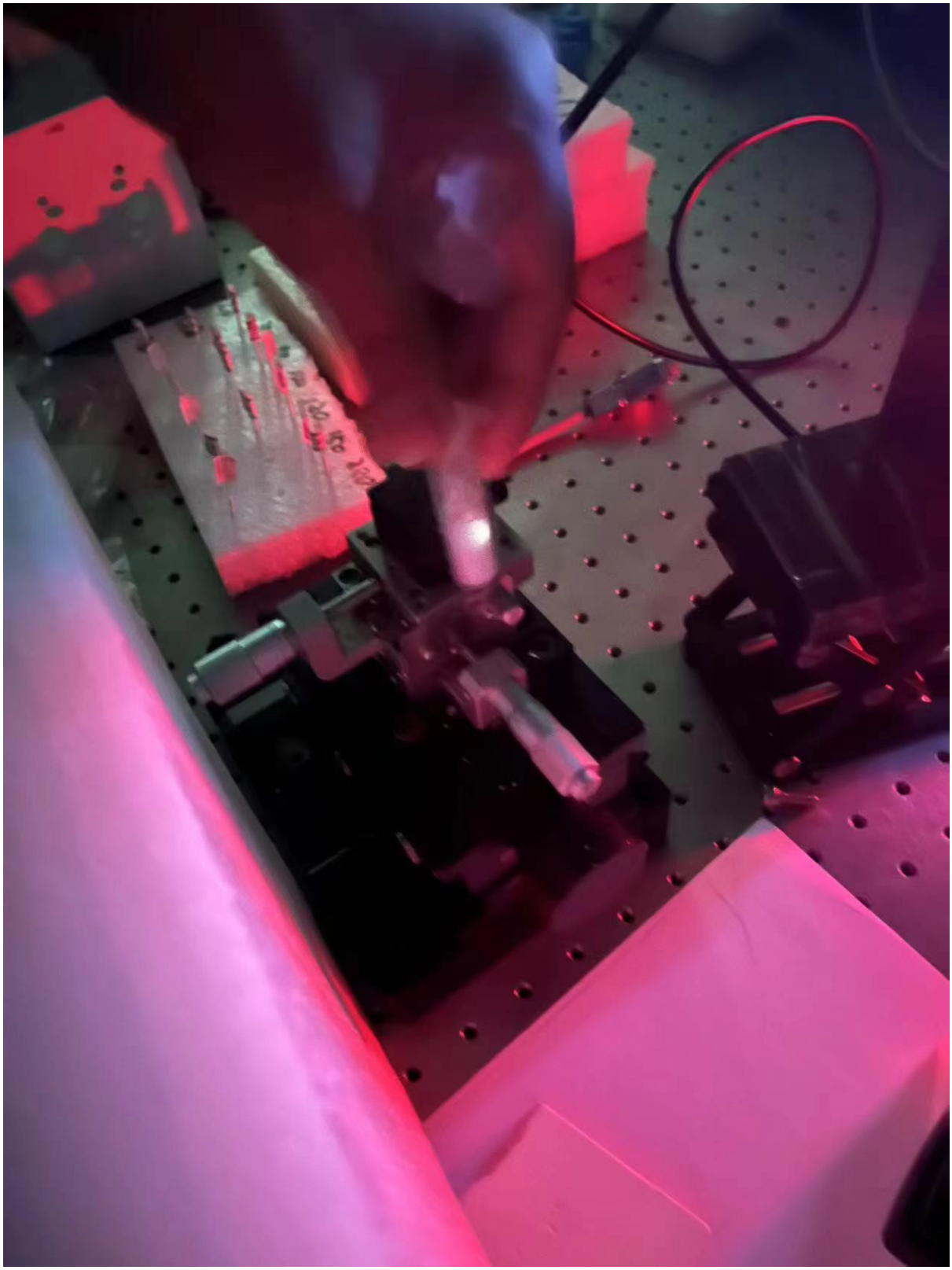

Figure S7. The SHG testing picture of $Na_6Si_3F_{18}$ crystal.