

## Supplementary Information

### **Na<sub>3</sub>Sc<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3</sub>: rational design and synthesis of alkali rare-earth phosphate fluoride as ultraviolet nonlinear optical crystal with an enlarged birefringence**

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Table S1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for NSPOF.

Atom	x	y	z	U(eq)
Sc(1)	0	0	7220(3)	7(1)
F(3)	0	0	9010(30)	32(6)
P(5)	0	-5000	7832(8)	13(1)
O(1)	0	-3150(20)	6944(12)	21(3)
O(2)	1870(20)	-5000	8629(13)	27(3)
F(2)	0	0	5300(30)	16(2)
F(1)	0	0	1554(18)	12(4)
Sc(2)	0	0	3457(3)	15(1)
Na(1)	2890(30)	0	10290(60)	53(3)
Na(1')	2213(10)	2213(10)	10322(19)	53(3)

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

Table S2. Selected bond lengths [ $\text{\AA}$ ] and angles [deg] for NSPOF.

P(5)-O(1)	1.552(13)	F(3)-Na(1)	2.36(4)
P(5)-O(2)	1.504(15)	F(3)-Na(1')	2.506(19)
Sc(1)-O(1)	2.103(13)	O(2)-P(5)-O(1)	110.83(17)
Sc(2)-O(2)#1	2.077(14)	O(2)#4-P(5)-O(2)	110.0(11)
Sc(1)-F(3)	1.94(3)	O(1)-P(5)-O(1)#4	103.4(11)
Sc(1)-F(2)	2.08(3)	F(2)-Sc(2)-F(1)	180.0
F(1)-Sc(2)	2.06(2)	F(3)-Sc(1)-O(1)#5	98.2(4)
F(1)-Na(1)#2	2.34(5)	F(2)-Sc(1)-O(1)#5	81.8(4)
F(1)-Na(1')#2	2.459(17)	O(1)#5-Sc(1)-O(1)#6	88.84(12)
F(2)-Sc(2)	1.99(3)	O(1)#5-Sc(1)-O(1)#7	163.6(8)
F(2)-Na(1')#3	2.601(10)	Sc(2)-F(2)-Sc(1)	180.0

Symmetry transformations used to generate equivalent atoms:

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

#4  $-x, -y-1, z$  #5  $y, -x, z$  #6  $-x, -y, z$  #7  $-y, x, z$

Table S3. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for NSPOF.

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

Atom	U11	U22	U33	U23	U13	U12
Sc(1)	3(1)	3(1)	14(3)	0	0	0
F(3)	37(8)	37(8)	22(10)	0	0	0
P(5)	11(2)	11(2)	17(1)	0	0	0
O(1)	35(6)	13(6)	16(6)	2(5)	0	0
O(2)	11(6)	43(8)	27(7)	0	1(6)	0
F(2)	21(3)	21(3)	7(4)	0	0	0
F(1)	18(5)	18(5)	1(7)	0	0	0
Sc(2)	20(2)	20(2)	5(2)	0	0	0
Na(1)	17(7)	118(13)	23(3)	0	-9(12)	0
Na(1')	17(7)	118(13)	23(3)	0	-9(12)	0

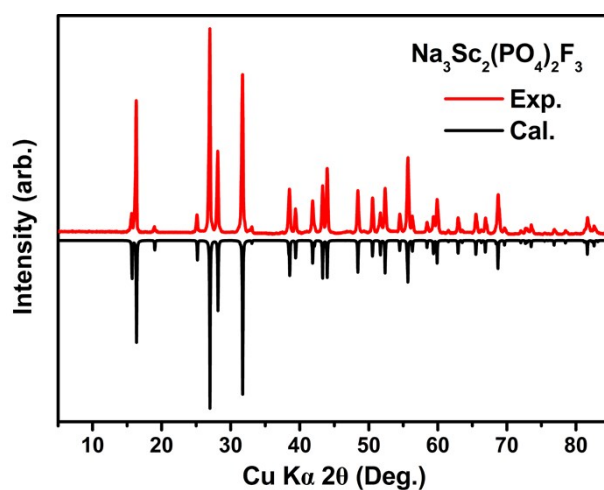


Figure S1. Calculated and experimental powder X-ray diffraction patterns of NSPOF.

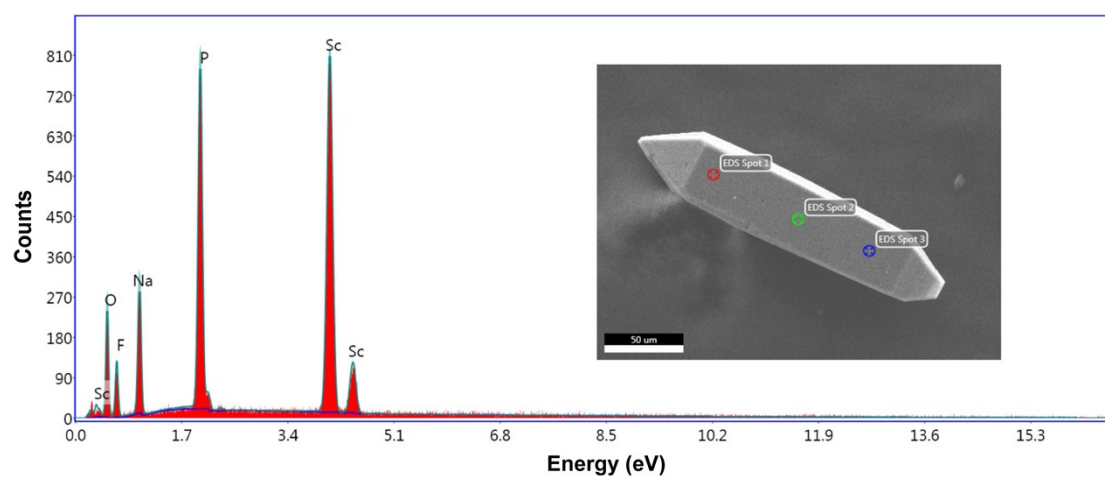


Figure S2. EDS analysis for NSPOF.

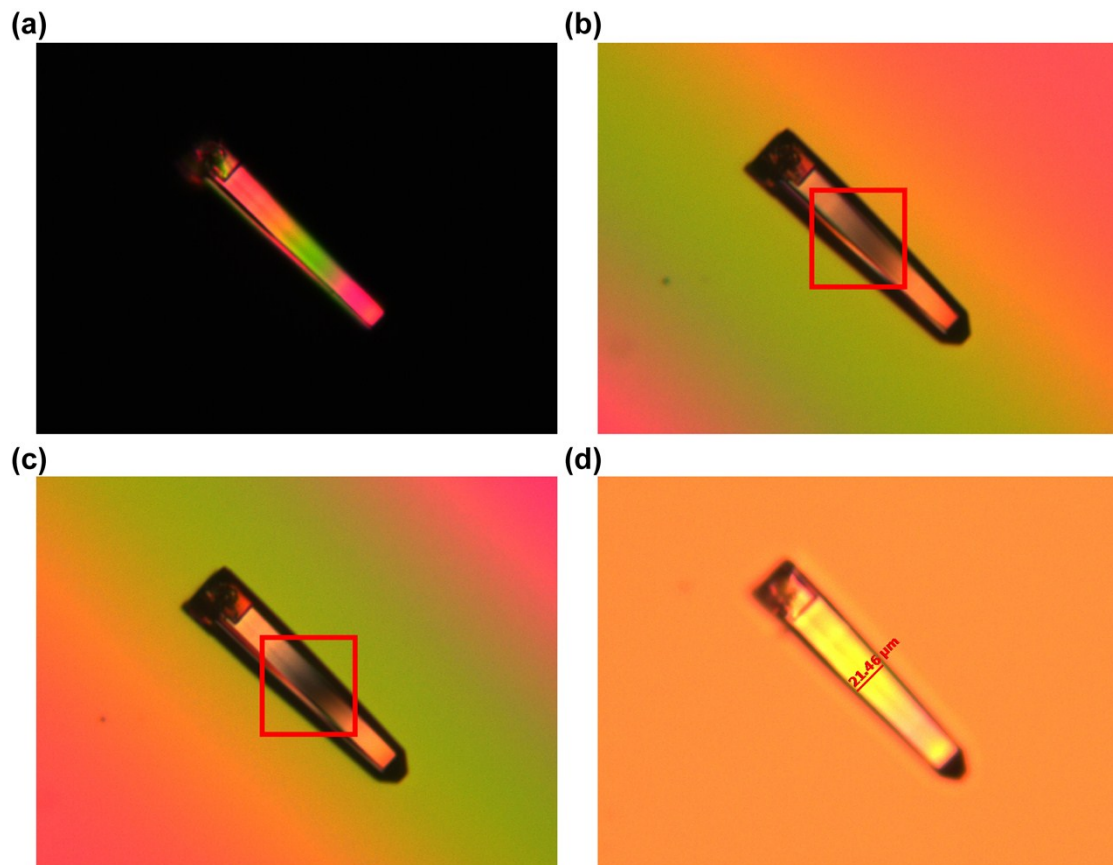


Figure S3. (a) Photograph of NSPOF for the measurement of birefringence, and (b) the positive and (c) negative rotation of compensatory, and (d) the thickness of measured NSPOF crystal.

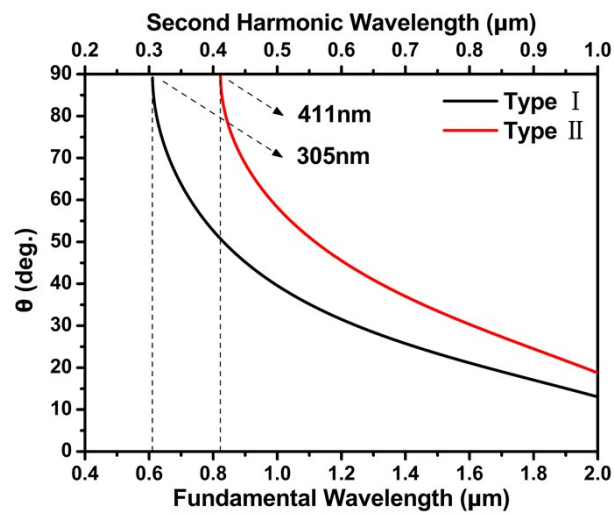


Figure S4. The phase-matching conditions of NSPOF.

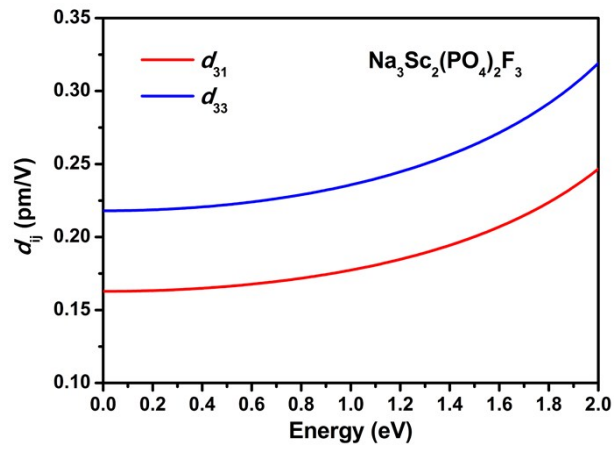


Figure S5. Calculated independent NLO coefficients of NSPOF.

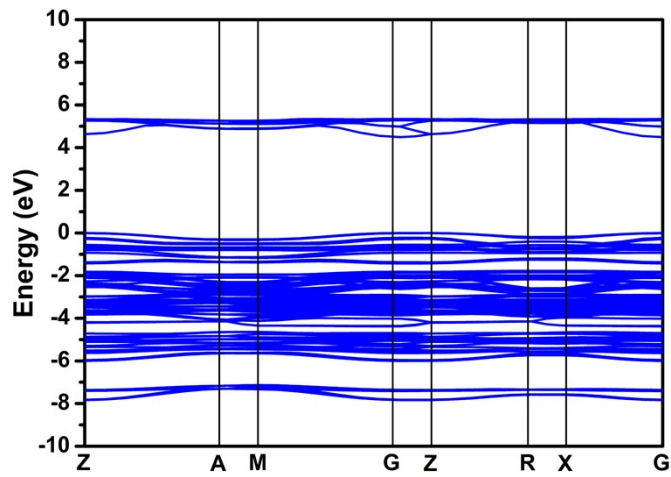


Figure S6. Calculated electronic band structure for NSPOF.

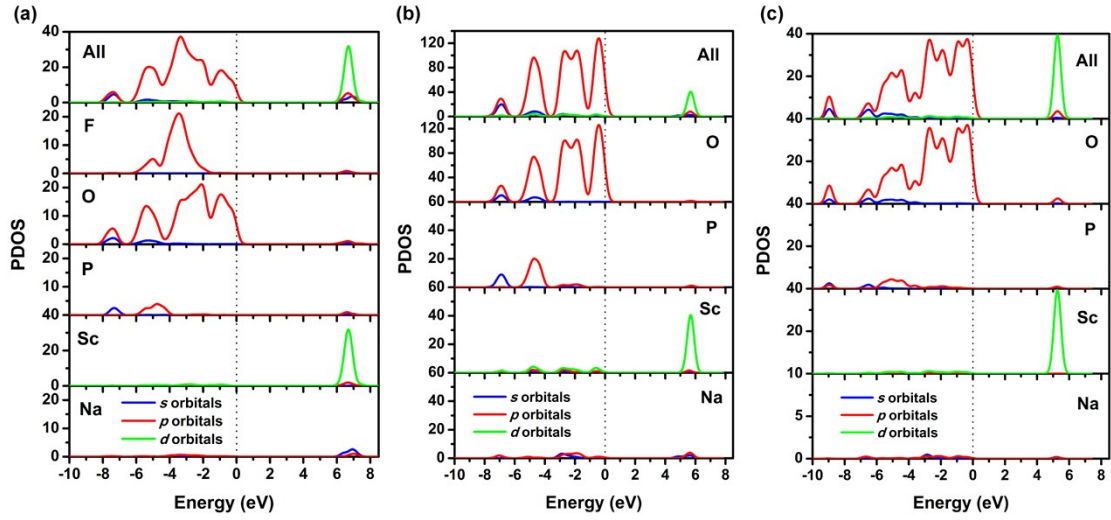


Figure S7. DOS and PDOS plots of (a) NSPOF, (b)  $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ , and (c)  $\text{NaScP}_2\text{O}_7$ .

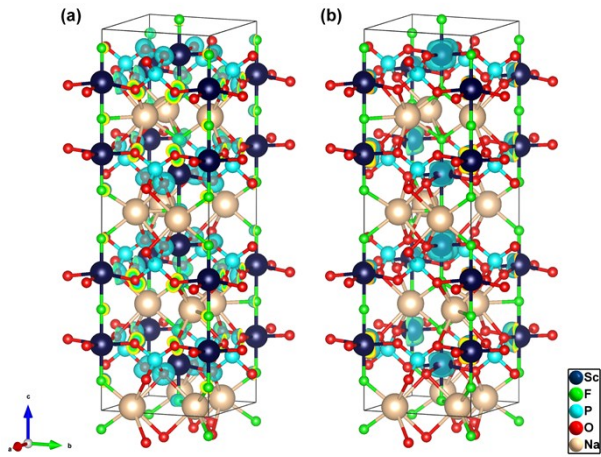


Figure S8. SHG density of (a) occupied and (b) unoccupied electronic states for NSPOF.

## The Anionic Group Theory Calculation

The macroscopic second-order susceptibility  $\chi^{(2)}$  can be expressed as

$$\chi_{ijk}^{(2)} = \frac{F}{V} \sum_P \sum_{i'j'k'} \alpha_{i'i'} \alpha_{j'j'} \alpha_{k'k'} \beta_{i'j'k'}^{(2)}(P), P = [\text{PO}_4]^{3-} \quad (\text{S1})$$

In this expression,  $F$  denotes the correction factor of localized field,  $V$  presents the volume of the unit cell,  $\alpha_{i'i'}$ ,  $\alpha_{j'j'}$ , and  $\alpha_{k'k'}$  denote the direction cosines between the macroscopic coordinate axes of the crystal and the microscopic coordinate axes of  $[\text{PO}_4]^{3-}$  groups, and  $\beta_{i'j'k'}$  shows the microscopic second-order susceptibility tensors of each group. Generally, the ideal  $[\text{PO}_4]^{3-}$  group is a tetrahedral group with point group  $D_{2d}$ , which has only one nonvanishing second-order susceptibility  $\beta_{123}^{(2)}$  on the basis of the Kleinman approximation. However, for NSPOF, the  $[\text{PO}_4]^{3-}$  groups are aberrant tetrahedrons with point group  $C_{4v}$ , which has two nonvanishing second-order susceptibility  $\beta_{311}^{(2)}$  and  $\beta_{333}^{(2)}$  according to the Kleinman approximation. Hence, the macroscopic second-order susceptibility, derived from the geometrical factor  $g$ , can be exhibited as

$$\chi_{ijk}^{(2)} = \frac{F}{V} \cdot (\mathbf{g}'_{ijk} \cdot \beta_{311}^{(2)} + \mathbf{g}''_{ijk} \cdot \beta_{333}^{(2)}); (i, j, k = 1, 2, 3) \quad (\text{S2})$$

$$\mathbf{g}'_{ijk} = \sum_P^n 2 \cdot [\alpha(i3)\alpha(j1)\alpha(k1) + \alpha(i1)\alpha(j3)\alpha(k1) + \alpha(i1)\alpha(j1)\alpha(k3)] \quad (\text{S3})$$

$$\mathbf{g}''_{ijk} = \sum_P^n [\alpha(i3)\alpha(j3)\alpha(k3)] \quad (\text{S4})$$

Here, the geometrical factor  $g$  can be derived from  $\mathbf{g}'_{ijk}$  and  $\mathbf{g}''_{ijk}$  according to the relationship between the two microscopic second-order susceptibility and the establishment of microscopic coordinate system for  $[\text{PO}_4]^{3-}$  groups, which is based on the symmetry. In the case of unspontaneous polarization, the structural criterion  $C$  is defined as

$$C = \frac{\mathcal{G}}{n} \quad (\text{S5})$$

Here,  $n$  denotes the number of anionic groups in a unit cell. Generally, the correction factor of localized field  $F$  is considered to be equal because of similar refractive indices. Therefore, the NLO coefficient is proportional to density of the  $[\text{PO}_4]^{3-}$  group ( $n/V$ ), the structural criterion ( $C$ ), and microscopic second-order susceptibility tensors based on the above derivation.