Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

$Na_6Sn_3P_4S_{16}$: Sn(II)-Chelated PS_4 groups inspired Ultra-strong SHG Response

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Table S1. Property comparison of the reported IR NLO thiophosphates with bandgaps (> 2.50 eV).

No.	Compounds	d_{ij}(×AGS)	E_g(eV)	Ref.
1	$Na_6Sn_3P_4S_{16}$	6.6	2.52	this work
2	$AgHgPS_4$	5	2.63	[1]
3	$KHgPS_4$	4.15	2.9	[2]
4	$Hg_3P_2S_8$	3.6	2.77	[3]
5	$NaHgPS_4$	3.14	2.78	[2]
6	$CuZnPS_4$	3	3	[4]
7	$Zn_3P_2S_8$	2.6	3.12	[5]
8	$KSbP_2S_6$	2.2	2.91	[6]
9	$K_2BaP_2S_6$	2.1	4.11	[6]
10	$AgZnPS_4$	1.8	2.76	[7]
11	α-$Ba_2P_2S_6$	1.7	4.31	[8]
12	$K_3YP_2S_8$	1.4	3.37	[9]
13	$Pb_2P_2S_6$	1.4	2.61	[8]
14	$KAg2PS_4$	1.4	2.92	[10]
15	$AgGa_2PS_6$	1	2.75	[11]

16	$Eu_2P_2S_6$	0.9	2.54	[12]
17	$LiZnPS_4$	0.8	3.38	[7]
18	$LiCd_3PS_6$	0.8	2.97	[13]
19	α-$Ag_4P_2S_6$	0.61	2.51	[14]
20	$LiGa_2PS_6$	0.5	3.15	[13]
21	$AgCd_3(PS_4)S_2$	0.45	2.56	[15]
22	$Rb_2Zn_3P_4S_{13}$	0.1	3.31	[16]
23	$Cs_2Zn_3P_4S_{13}$	0.1	3.29	[16]

Table S2. Crystal data and structure refinement for $Na_6Sn_3P_4S_{16}$.

Empirical formula	$Na_6Sn_3P_4S_{16}$
formula weight	1130.85
crystal system	trigonal
space group	*R*3*m*
cell parameter *a* (Å)	19.304(4)
cell parameter *c* (Å)	6.181(2)
Z, *V* (Å^3) (Volume)	3, 1994.6(11)
D_c (g/cm^3) (calculated density)	2.824
μ (mm^{-1}) (absorption coefficient)	4.388
goodness-of-fit on F^2	0.998
R_1, wR_2 ($I > 2\sigma(I)$)[a]	0.0427, 0.0629,
R_1, wR_2 (all data)	0.0724, 0.0783
absolute structure parameter	-0.03(6)

[a]$R_1 = F_o - F_c / F_o$ and $wR_2 = [w (F_o^2 - F_c^2)^2 / wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma (F_o^2)$

Table S3. The coordination modes of Sn(II) in the known chalcogenide compounds.

Compounds	Space group	Link modes
$Sn_2Ga_2S_5$	*Pna*2$_1$	SnS_4
$SnGa_4S_7$	*Pc*	SnS_4
$BaSnS_2$	*P*-1	SnS_3
$BaSn_2S_3$	*P*-1	SnS_3
$Ag_4SnGe_2S_7$	*Cc*	SnS_3
$Ag_7Sn(PS_4)_3$	*P*2$_1$/*c*	SnS_3
$KSnPS_4$	*P*2$_1$/*c*	SnS_3
$CsSnPS_4$	*P*2$_1$/*m*	SnS_3
$SnGa_2GeS_6$	*Fdd*2	SnS_5
$LaSnGa_3S_7$	*P*2$_1$/n	SnS_5
Sn_2SiS4	*P*21/*c*	SnS_6
$SnPS_3$	*Pn*	SnS_8

Table S4. Dipole moment calculation for $Na_6Sn_3P_4S_{16}$.

Dipole Moment					
Species	**x(a)**	**y(b)**	**z(c)**	**Magnitude**	
				Debye	**×10^{-4}esu·cm/Å^3**
$Na_6Sn_3P_4S_{16}$					
NaS_6	-1.89	1.88	11.48	11.79	0.02
SnS_4	-38.03	38.03	-123.76	134.94	0.20
$P(1)S_4$	38.51	-38.11	-5.38	54.45	0.08
$P(2)S_4$	57.26	-57.26	19.05	83.19	0.13
Unit Cell	55.85	-55.46	-98.61	284.37	0.43

2. Figures

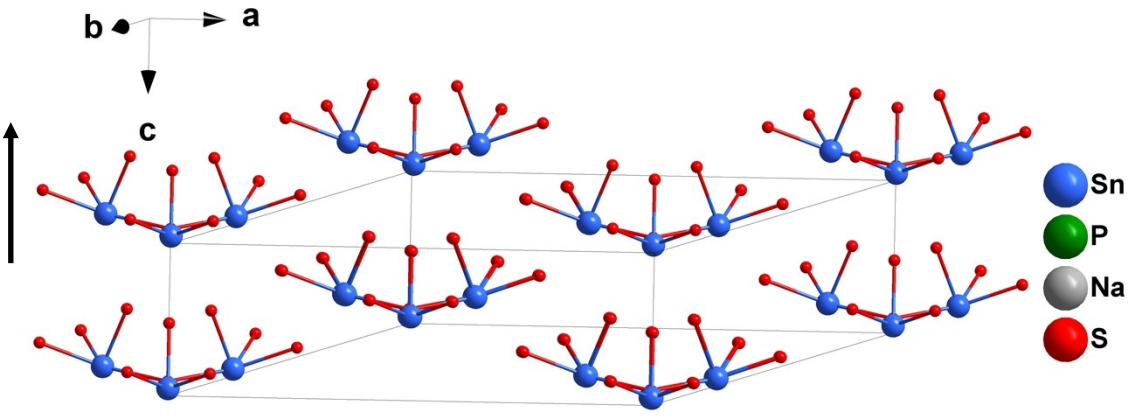

Figure S1. The overall stacking arrangement of SnS_4 units in the unit cell in $Na_6Sn_3P_4S_{16}$.

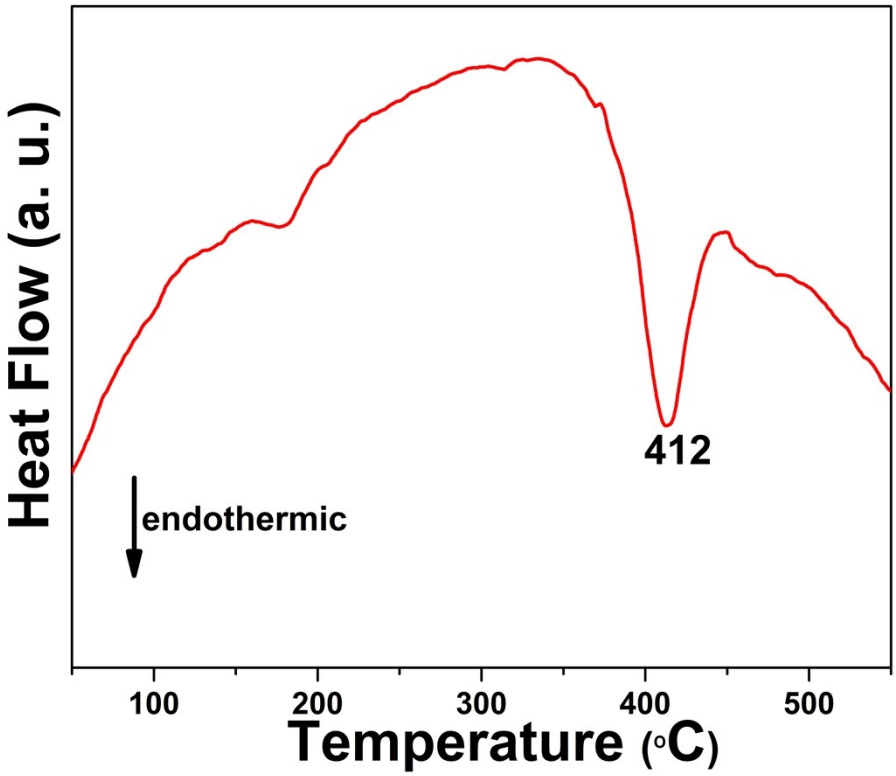

Figure S2. DSC curve of $Na_6Sn_3P_4S_{16}$.

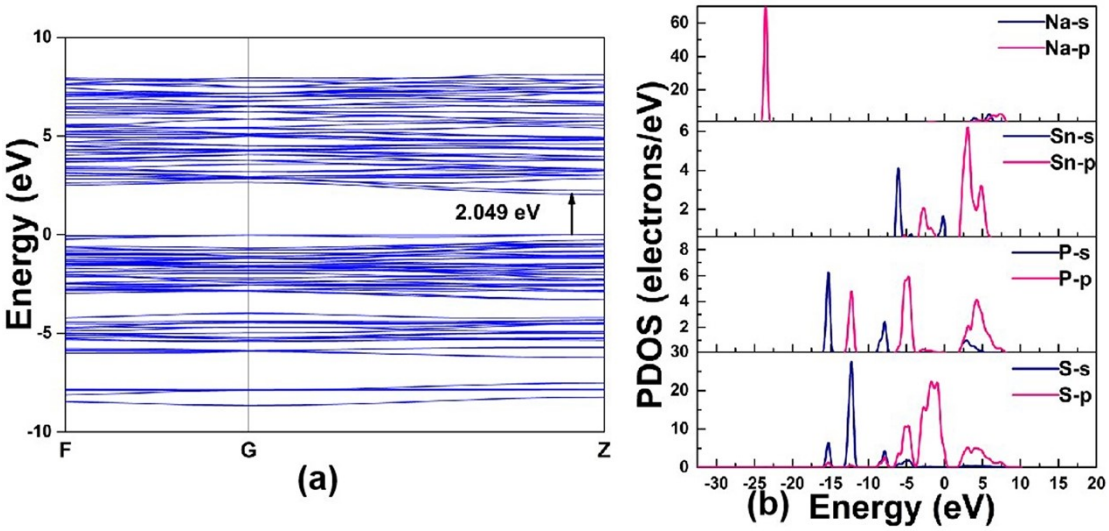

Figure S3. Band structure and DOS diagram of $Na_6Sn_3P_4S_{16}$.

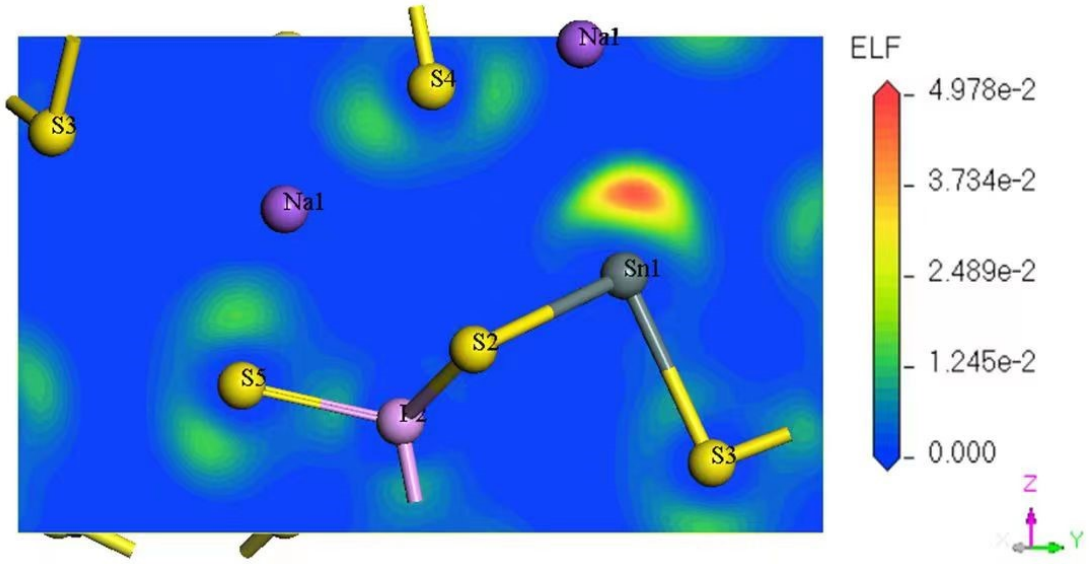

Figure S4. ELF map of $Na_6Sn_3P_4S_{16}$.

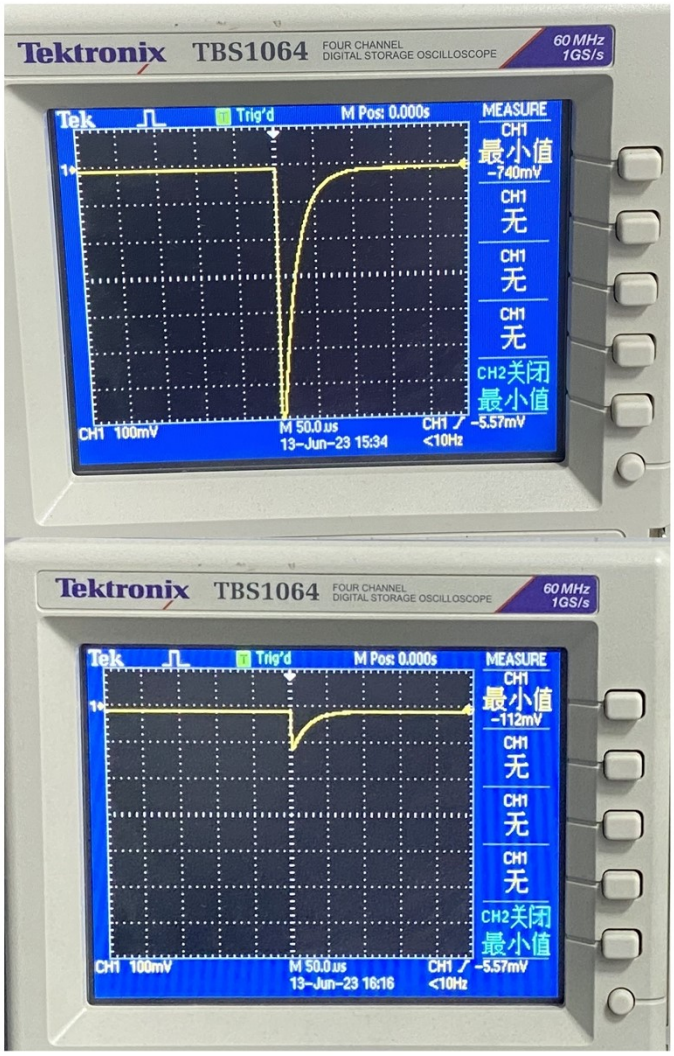

Figure S5. Experimental SHG intensity of the $Na_6Sn_3P_4S_{16}$ and the standard $AgGaS_2$ at the particle size (200-250 μm).

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