

Electronic Supporting Information

Na₄Sn₄(C₂O₄)₃F₆ and NaSnC₂O₄F·H₂O: two tin(II) fluoride oxalates display large birefringence

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Table of contents

Sections	Titles	Pages
Table S1	Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Na}_4\text{Sn}_4(\text{C}_2\text{O}_4)_3\text{F}_6$. $U_{(\text{eq})}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.	S3
Table S2	Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{NaSnC}_2\text{O}_4\text{F} \cdot \text{H}_2\text{O}$. $U_{(\text{eq})}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.	S4
Table S3	Selected bond lengths [\AA] and angles [$^\circ$] for $\text{Na}_4\text{Sn}_4(\text{C}_2\text{O}_4)_3\text{F}_6$.	S5
Table S4	Selected bond lengths [\AA] and angles [$^\circ$] for $\text{NaSnC}_2\text{O}_4\text{F} \cdot \text{H}_2\text{O}$.	S6
Fig. S1	Powder XRD patterns of $\text{Na}_4\text{Sn}_4(\text{C}_2\text{O}_4)_3\text{F}_6$ and $\text{NaSnC}_2\text{O}_4\text{F} \cdot \text{H}_2\text{O}$.	S7
Fig. S2	The TG curves of $\text{Na}_4\text{Sn}_4(\text{C}_2\text{O}_4)_3\text{F}_6$ and $\text{NaSnC}_2\text{O}_4\text{F} \cdot \text{H}_2\text{O}$.	S7
Fig. S3	XRD patterns for compounds $\text{Na}_4\text{Sn}_4(\text{C}_2\text{O}_4)_3\text{F}_6$ and $\text{NaSnC}_2\text{O}_4\text{F} \cdot \text{H}_2\text{O}$ after melting.	S7
Fig. S4	IR spectra of $\text{Na}_4\text{Sn}_4(\text{C}_2\text{O}_4)_3\text{F}_6$ and $\text{NaSnC}_2\text{O}_4\text{F} \cdot \text{H}_2\text{O}$.	S8
Fig. S5	The UV-vis-NIR diffuse reflectance spectra and band gaps of $\text{Na}_4\text{Sn}_4(\text{C}_2\text{O}_4)_3\text{F}_6$ and $\text{NaSnC}_2\text{O}_4\text{F} \cdot \text{H}_2\text{O}$.	S8
Fig. S6	Birefringence measurement photos of $\text{Na}_4\text{Sn}_4(\text{C}_2\text{O}_4)_3\text{F}_6$ and $\text{NaSnC}_2\text{O}_4\text{F} \cdot \text{H}_2\text{O}$.	S8
Fig. S7	Calculated band gaps of $\text{Na}_4\text{Sn}_4(\text{C}_2\text{O}_4)_3\text{F}_6$ and $\text{NaSnC}_2\text{O}_4\text{F} \cdot \text{H}_2\text{O}$.	S9

Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Na}_4\text{Sn}_4(\text{C}_2\text{O}_4)_3\text{F}_6$. $U_{(\text{eq})}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
Sn1	8305.4(3)	11381.0(2)	1343.7(2)	18.54(7)
Sn2	8318.5(3)	5688.7(2)	8202.9(2)	20.15(7)
Na1	8604(2)	7352.8(14)	3758.5(14)	25.9(3)
Na2	12912(2)	9569.1(15)	4212.6(15)	29.6(3)
F1	6385(3)	10415(2)	3438.6(19)	30.5(4)
F2	10601(3)	9563(2)	2571(2)	29.6(4)
F3	8686(3)	7646(2)	6176(2)	33.5(4)
O1	5403(3)	2967(2)	6078(3)	23.2(4)
O2	7879(3)	4206(2)	6773(3)	25.1(4)
O3	7533(3)	9240(2)	834(2)	22.6(4)
O4	2013(3)	4769(3)	7154(3)	25.9(4)
O5	4565(4)	5915(3)	7896(3)	28.5(5)
O6	5471(4)	8154(3)	-329(3)	33.1(5)
C1	5890(5)	3931(3)	6663(3)	18.1(5)
C2	5853(5)	9253(3)	139(3)	19.1(6)
C3	3971(5)	4971(3)	7289(3)	18.8(5)

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{NaSnC}_2\text{O}_4\text{F} \cdot \text{H}_2\text{O}$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
Sn1	10808.2(4)	7335.9(3)	9565.1(3)	23.32(10)
Na1	9074(3)	2384(2)	5096(2)	28.9(3)
F1	9720(4)	4253(3)	8203(3)	28.1(5)
O1	8639(5)	7385(4)	6887(3)	25.2(5)
O2	4999(5)	7417(4)	5116(4)	29.9(6)
O3	6842(5)	7004(4)	9355(3)	29.7(6)
O4	3099(5)	6682(5)	7450(4)	34.1(6)
O5	7518(6)	-1233(5)	3303(4)	33.3(7)
C1	5316(7)	6951(5)	7879(5)	23.9(7)
C2	6369(6)	7276(5)	6482(5)	21.2(7)

Table S3. Selected bond lengths [Å] and angles [°] for Na₄Sn₄(C₂O₄)₃F₆.

Sn1-F1	2.0439(17)	Na1-O4 ^v	2.381(2)
Sn1-F2	2.0989(16)	Na2-F1 ⁱⁱ	2.243(2)
Sn1-O3	2.2092(19)	Na2-F1 ^{iv}	2.251(2)
Sn1-O6 ⁱ	2.521(2)	Na2-F2	2.194(2)
Sn2-F3	2.0473(17)	Na2-F3 ^{iv}	2.447(2)
Sn2-O2	2.204(2)	Na2-O1 ^{vi}	2.424(2)
Sn2-O4 ⁱⁱ	2.454(2)	O1-C1	1.232(3)
Sn2-O5	2.301(2)	O2-C1	1.278(3)
Na1-F1	2.800(2)	O3-C2	1.271(3)
Na1-F2	2.266(2)	O4-C3	1.246(3)
Na1-F3	2.318(2)	O5-C3	1.258(3)
Na1-O1 ^v	2.446(2)	O6-C2	1.243(4)
Na1-O2 ^{vi}	2.466(2)	C1-C3	1.555(4)
Na1-O3	2.731(2)	C2-C2 ⁱ	1.539(5)
F1-Sn1-F2	79.55(8)	O1 ^{vi} -Na2-F3 ^{iv}	166.39(9)
F2-Sn1-O3	77.87(7)	Sn1-F1-Na1	89.82(7)
F2-Sn1-O6 ⁱ	143.06(7)	Sn1-F1-Na2 ⁱⁱⁱ	136.43(9)
O3-Sn1-O6 ⁱ	69.12(7)	Na2-F2-Na1	107.07(8)
F3-Sn2-O2	88.70(8)	Na2 ^{vi} -O1-Na1 ^v	101.91(8)
O5-Sn2-O4 ⁱⁱ	141.72(7)	C1-O1-Na1 ^v	116.08(18)
F2-Na1-F1	62.06(7)	C1-O1-Na2 ^{vi}	135.79(18)
F2-Na1-O2 ^{vi}	85.04(8)	Sn2-O2-Na1 ^{vi}	111.88(9)
F3-Na1-F1	75.98(6)	C1-O2-Sn2	118.76(18)
F3-Na1-O3	137.89(8)	Sn1-O3-Na1	88.30(7)
O2 ^{vi} -Na1-F1	147.07(8)	C2-O3-Sn1	122.48(17)
O2 ^{vi} -Na1-O3	103.84(8)	C3-O4-Sn2 ⁱⁱⁱ	133.04(19)
O3-Na1-F1	62.62(6)	C2-O6-Sn1 ⁱ	112.68(18)
O4 ^v -Na1-O2 ^{vi}	67.60(7)	O1-C1-C3	118.9(2)
O4 ^v -Na1-O3	81.90(7)	O2-C1-C3	115.3(2)
F1 ^{iv} -Na2-O1 ^{vi}	107.59(8)	O6-C2-O3	125.2(3)
F2-Na2- F1 ^{iv}	151.79(10)	O4-C3-O5	126.9(3)
F2-Na2-F1 ⁱⁱ	123.35(9)		

Symmetry codes:

(i) 1-x, 2-y, -z; (ii) 1+x, +y, +z; (iii) -1+x, +y, +z; (iv) 2-x, 2-y, 1-z; (v) 1-x, 1-y, 1-z; (vi) 2-x, 1-y, 1-z; (vii) 3-x, 2-y, 1-z.

Table S4. Selected bond lengths [Å] and angles [°] for NaSnC₂O₄F·H₂O.

Sn1-F1	2.020(2)	Na1-O5	2.390(3)
Sn1-O1	2.215(3)	O1-Na1 ⁱⁱ	2.479(3)
Sn1-O3	2.304(3)	O1-C2	1.280(4)
Sn1-O4 ⁱ	2.496(2)	O2-C2	1.223(4)
Na1-F1	2.318(2)	O3-C1	1.266(5)
Na1-O2 ^{iv}	2.416(3)	O4-C1	1.234(5)
Na1-O4 ^{iv}	2.480(3)	C1-C2	1.551(5)
F1-Sn1-O1	86.59(9)	C2-O1-Sn1	119.0(2)
F1-Sn1-O4 ⁱ	78.50(9)	C2-O1-Na1 ⁱⁱⁱ	125.8(2)
O1-Sn1-O4 ⁱ	69.91(9)	Na1 ^{iv} -O4-Sn1 ^v	105.65(11)
O3-Sn1-O4 ⁱ	138.82(9)	C1-O4-Sn1 ^v	128.1(2)
F1-Na1-O1 ⁱⁱⁱ	133.55(11)	C1-O4-Na1 ^{iv}	116.2(2)
F1-Na1-O2 ^{iv}	78.67(10)	Na1-O5-Na1 ⁱⁱ	99.52(12)
O1 ⁱⁱⁱ -Na1-O4 ^{iv}	66.23(9)	O3-C1-C2	116.0(3)
O1 ⁱⁱⁱ -Na1-O5 ⁱⁱ	85.60(11)	O4-C1-O3	126.8(3)
O2 ^{iv} -Na1-O1 ⁱⁱⁱ	132.82(10)	O4-C1-C2	117.2(3)
O4 ^{iv} -Na1-O5 ⁱⁱ	151.56(12)	O1-C2-C1	115.9(3)
O5-Na1-O4 ^{iv}	95.66(12)	O2-C2-O1	125.8(3)
Sn1-F1-Na1	125.40(10)	O2-C2-C1	118.3(3)

Symmetry codes:

- (i) 1+x, +y, +z; 3/2-z; (ii) 2-x, 1-y, 1-z; (iii) 2-x, -y, 1-z; (iv) 1-x, 1-y, 1-z; (v) -1+x, +y, +z.
(i) 1+x, +y, +z; (ii) 2-x, -y, 1-z; (iii) 2-x, 1-y, 1-z; (iv) 1-x, 1-y, 1-z; (v) -1+x, +y, +z.

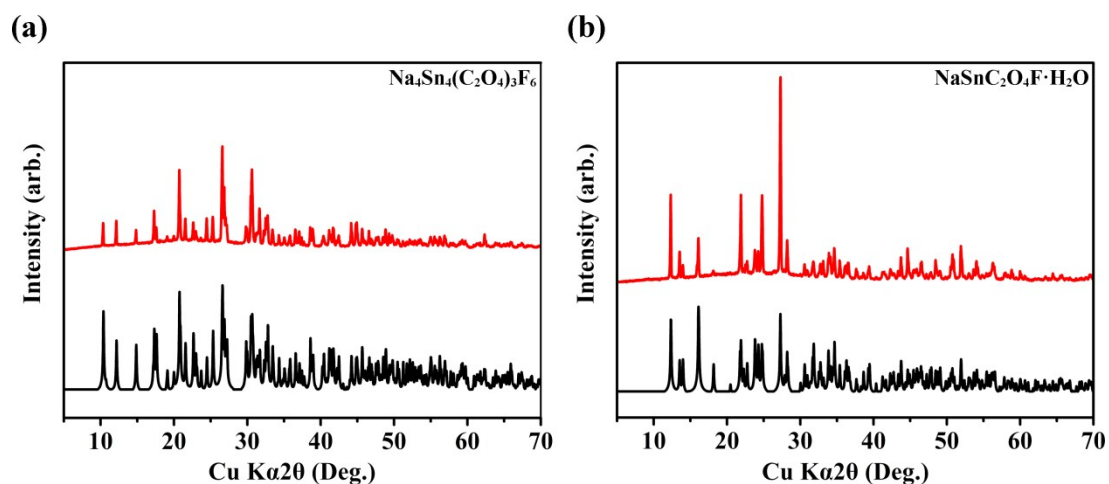


Fig. S1 Powder XRD patterns of (a) $\text{Na}_4\text{Sn}_4(\text{C}_2\text{O}_4)_3\text{F}_6$ and (b) $\text{NaSnC}_2\text{O}_4\text{F}\cdot\text{H}_2\text{O}$. The red curves are patterns of samples, the black are the simulated ones.

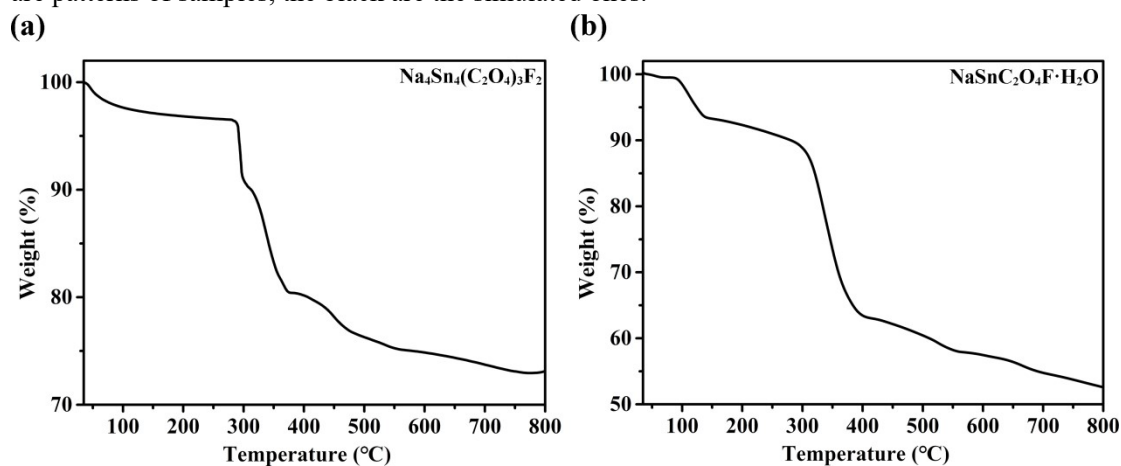


Fig. S2 The TG curves of (a) $\text{Na}_4\text{Sn}_4(\text{C}_2\text{O}_4)_3\text{F}_6$ and (b) $\text{NaSnC}_2\text{O}_4\text{F}\cdot\text{H}_2\text{O}$.

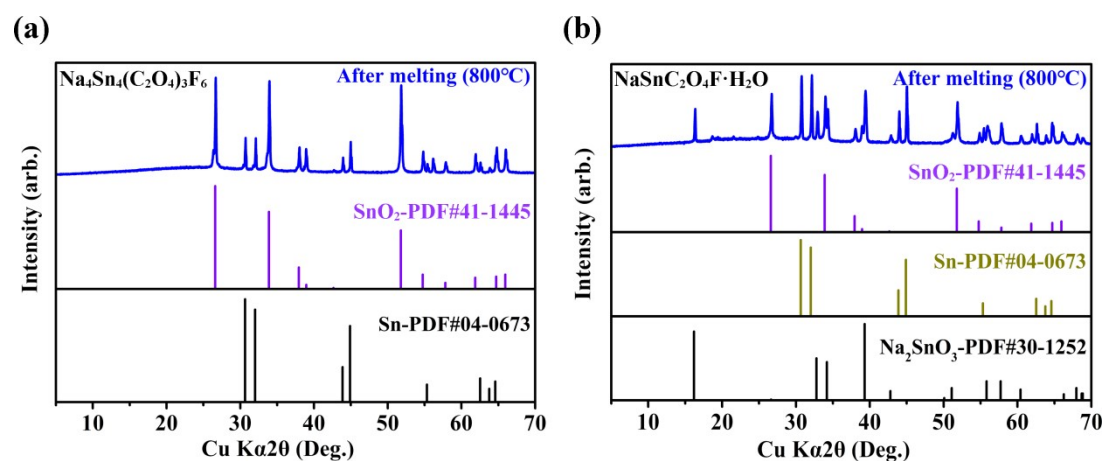


Fig. S3 XRD patterns for compounds (a) $\text{Na}_4\text{Sn}_4(\text{C}_2\text{O}_4)_3\text{F}_6$ and (b) $\text{NaSnC}_2\text{O}_4\text{F}\cdot\text{H}_2\text{O}$ after melting.

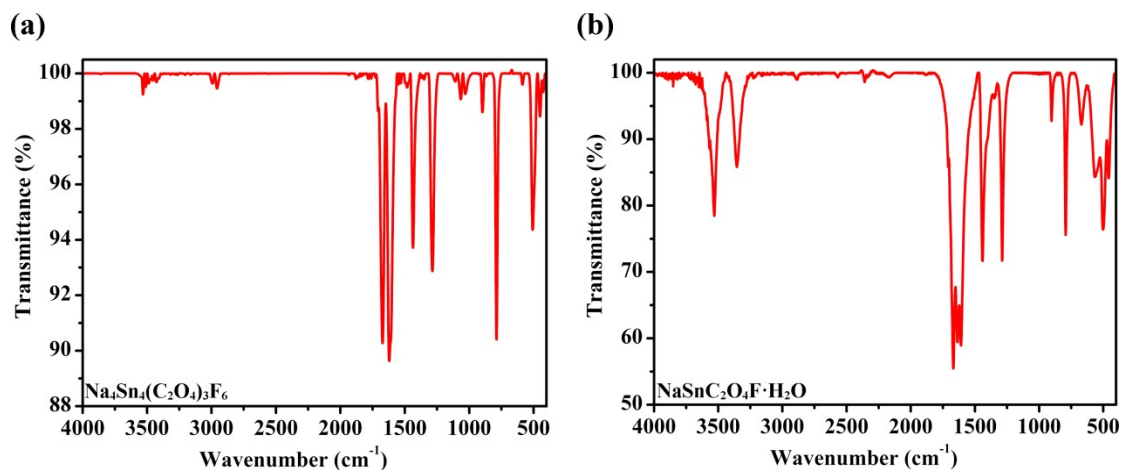


Fig. S4 IR spectra of (a) $\text{Na}_4\text{Sn}_4(\text{C}_2\text{O}_4)_3\text{F}_6$ and (b) $\text{NaSnC}_2\text{O}_4\text{F}\cdot\text{H}_2\text{O}$.

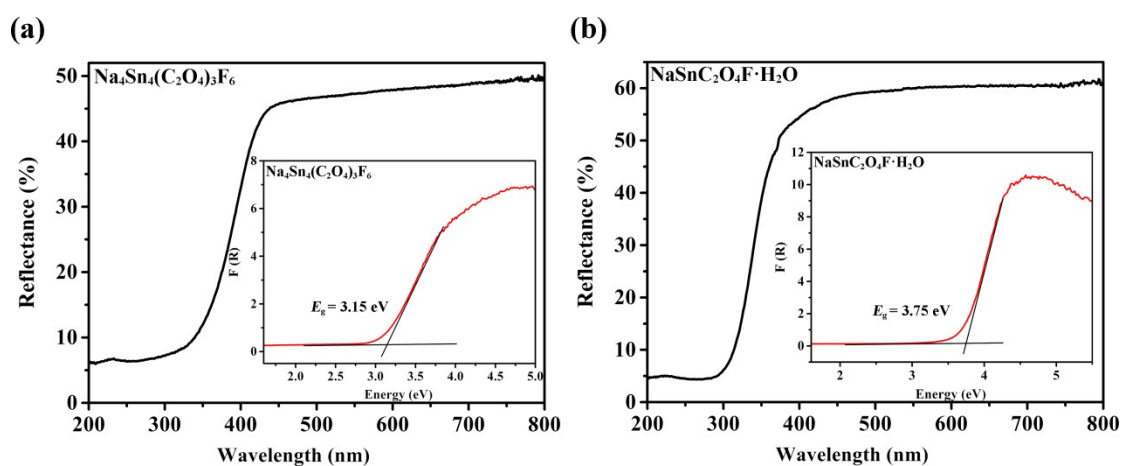


Fig. S5 The UV-vis-NIR diffuse reflectance spectra and band gaps of (a) $\text{Na}_4\text{Sn}_4(\text{C}_2\text{O}_4)_3\text{F}_6$ and (b) $\text{NaSnC}_2\text{O}_4\text{F}\cdot\text{H}_2\text{O}$.

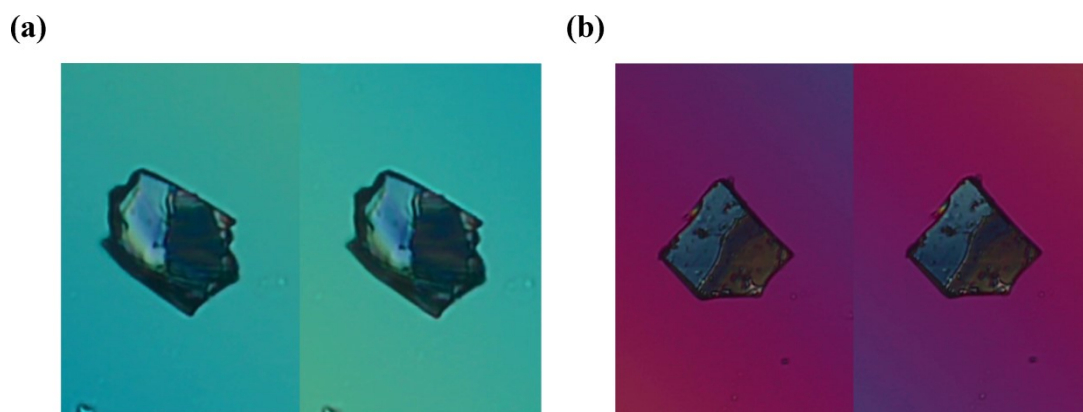


Fig. S6 Birefringence measurement photos of (a) $\text{Na}_4\text{Sn}_4(\text{C}_2\text{O}_4)_3\text{F}_6$ and (b) $\text{NaSnC}_2\text{O}_4\text{F}\cdot\text{H}_2\text{O}$.

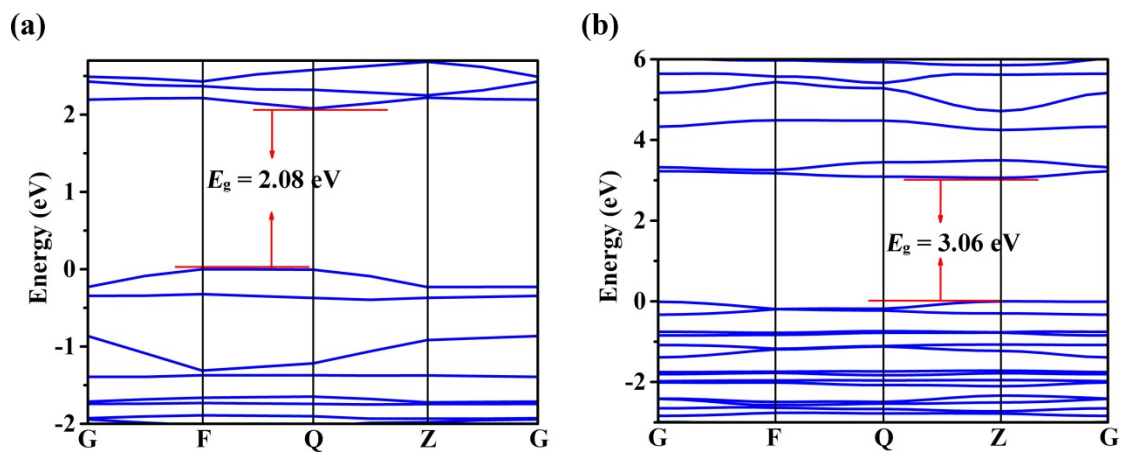


Fig. S7 Calculated band gaps of (a) $\text{Na}_4\text{Sn}_4(\text{C}_2\text{O}_4)_3\text{F}_6$ and (b) $\text{NaSnC}_2\text{O}_4\text{F}\cdot\text{H}_2\text{O}$.