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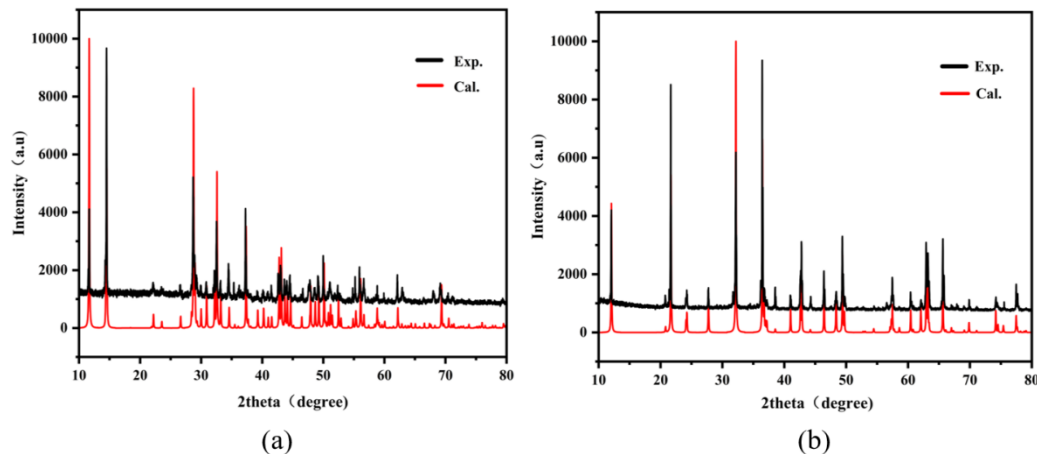


Figure S1: Experimental (black) and simulated (red) PXRD of $\text{Na}_6\text{ZnF}_2(\text{B}_{12}\text{O}_{24})\text{H}_6$ (a), $\text{KZn}_3\text{F}(\text{BO}_3)_2$ (b).

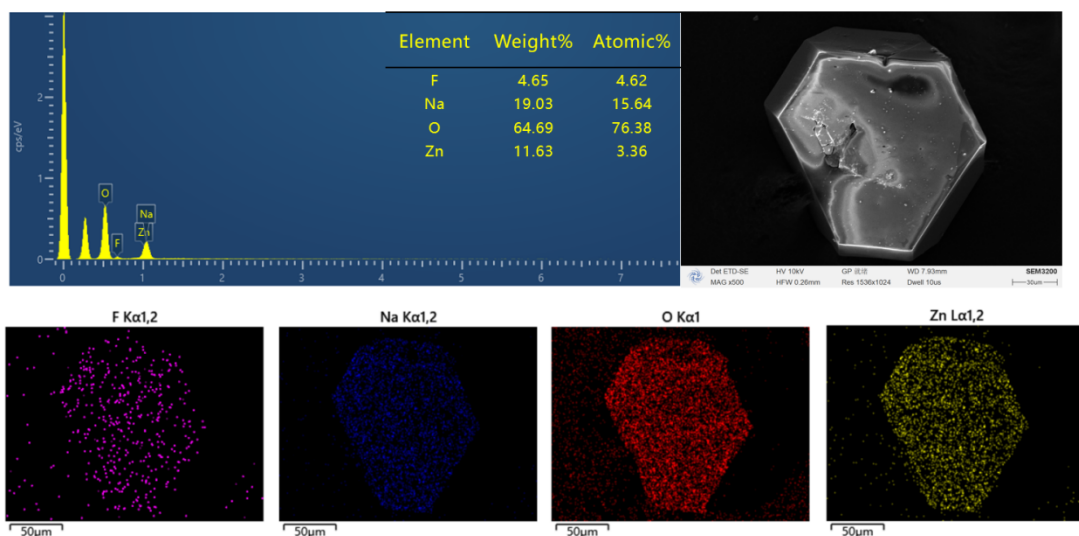


Figure S2: EDX and SEM images of $\text{Na}_6\text{ZnF}_2(\text{B}_{12}\text{O}_{24})\text{H}_6$.

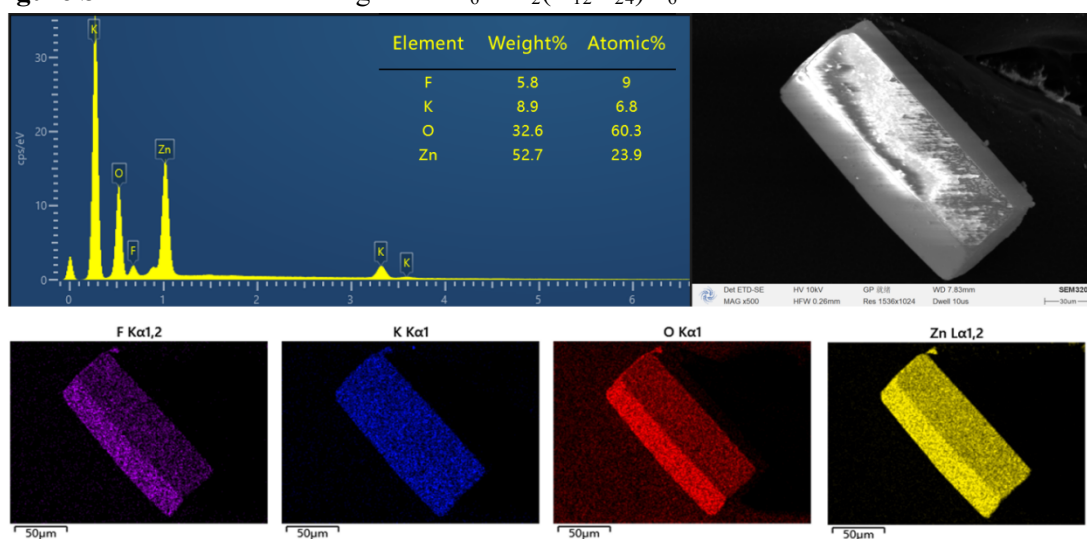


Figure S3: EDX and SEM images of $\text{KZn}_3\text{F}(\text{BO}_3)_2$.

Table S1: Important Bond Lengths (angstroms) and Important Bond angles (degrees) for $\text{Na}_6\text{ZnF}_2(\text{B}_{12}\text{O}_{24})\text{H}_6$ and $\text{KZn}_3\text{F}(\text{BO}_3)_2$

$\text{Na}_6\text{ZnF}_2(\text{B}_{12}\text{O}_{24})\text{H}_6$		$\text{KZn}_3\text{F}(\text{BO}_3)_2$	
Zn(1)-O(3)	2.032(6)	Zn(1)-O(1)	2.1281(18)
Zn(1)-O(3)	2.032(6)	Zn(1)-O(1)	2.1281(18)
Zn(1)-O(3)	2.032(6)	Zn(1)-O(1)	2.1281(18)
Zn(1)-F(1)	1.762(12)	Zn(1)-O(1)	2.1281(18)
Na(1)-O(2)	2.522(6)	Zn(1)-O(1)	2.1281(18)
Na(1)-O(2)	2.522(6)	Zn(1)-O(1)	2.1281(18)
Na(1)-O(2)	2.522(6)	B(1)-O(1)	1.3795(19)
Na(1)-O(4)	2.566(6)	B(1)-O(1)	1.3795(19)
Na(1)-O(4)	2.566(6)	B(1)-O(1)	1.3795(19)
Na(1)-O(4)	2.566(6)	Zn(2)-O(1)	1.9303(19)

Na(1)-F(1)	2.313(13)	Zn(2)-O(1)	1.9303(19)
Na(2)-O(1)	2.403(7)	Zn(2)-O(1)	1.9303(19)
Na(2)-O(1)	2.403(7)	Zn(2)-F(1)	2.0203(5)
Na(2)-O(3)	2.592(6)	K(1)-F(1)	2.84280(12)
Na(2)-O(3)	2.592(6)	K(1)-F(1)	2.84280(11)
Na(2)-O(4)	2.397(6)	K(1)-F(1)	2.84281(11)
Na(2)-O(4)	2.397(6)	K(1)-O(1)	2.9056(18)
Na(2)-F(1)	2.8795(17)	K(1)-O(1)	2.9056(18)
Na(2)-F(1)	2.8795(17)	K(1)-O(1)	2.9056(18)
B(2)-O(1)	1.365(10)	K(1)-O(1)	2.9056(18)
B(1)-O(2)	1.488(9)	K(1)-O(1)	2.9056(18)
B(1)-O(3)	1.442(9)		
B(1)-O(3)	1.493(10)	O(1)-Zn(1)-O(1)	86.65(7)
B(1)-O(4)	1.452(9)	O(1)-Zn(1)-O(1)	93.35(7)
B(2)-O(2)	1.348(10)	O(1)-Zn(1)-O(1)	180.00(7)
B(2)-O(4)	1.367(10)	O(1)-Zn(1)-O(1)	86.65(7)
		O(1)-Zn(1)-O(1)	86.65(7)
O(3)-Zn(1)-O(3)	115.62(12)	O(1)-Zn(1)-O(1)	93.35(7)
O(3)-Zn(1)-O(3)	115.62(12)	O(1)-Zn(1)-O(1)	93.35(7)
O(3)-Zn(1)-O(3)	115.62(12)	O(1)-Zn(1)-O(1)	86.65(7)
F(1)-Zn(1)-O(3)	102.25(18)	O(1)-Zn(1)-O(1)	180.0
F(1)-Zn(1)-O(3)	102.25(17)	O(1)-Zn(1)-O(1)	93.35(7)
F(1)-Zn(1)-O(3)	102.25(17)	O(1)-Zn(1)-O(1)	86.65(7)
O(2)-B(1)-O(3)	108.6(6)	O(1)-B(1)-O(1)	120.000(2)
O(3)-B(1)-O(2)	110.0(6)	O(1)-B(1)-O(1)	120.000(2)
O(3)-B(1)-O(3)	110.2(7)	O(1)-B(1)-O(1)	120.000(2)
O(3)-B(1)-O(4)	109.1(6)	O(1)-Zn(2)-O(1)	116.86(3)
O(4)-B(1)-O(2)	107.6(6)	O(1)-Zn(2)-O(1)	116.86(3)
O(4)-B(1)-O(3)	111.2(6)	O(1)-Zn(2)-O(1)	116.86(3)
O(1)-B(2)-O(4)	116.7(7)	O(1)-Zn(2)-F(1)	100.33(5)
O(1)-B(2)-O(1)	120.6(7)	O(1)-Zn(2)-F(1)	100.33(5)
O(1)-B(2)-O(4)	122.7(7)	O(1)-Zn(2)-F(1)	100.33(5)

Na₆ZnF₂(B₁₂O₂₄)H₆. Symmetry transformations used to generate equivalent atoms:

#1 -x+4/3, -y+2/3, -z+2/3; #2 y-1/3, x-2/3, -z+5/6; #3 -x+1, -y+1, -z+1; #4 -y+1, x-y, z; #5 -x+y+1, -x+1, z; #6 x-1/3, x-y+1/3, z-1/6; #7 x-y, x, -z+1; #8 y+2/3, x+1/3, -z+5/6; #9 -y+2/3, -x+1/3, z-1/6; #10 x-y+2/3, -y+1/3, -z+5/6; #11 -x+y+2/3, y+1/3, z-1/6; #12 -x+2/3, -x+y+1/3, -z+5/6; #13 x+2/3, x-y+1/3, z-1/6; #14 y, -x+y, -z+1; #15 -y+1/3, -x+2/3, z+1/6.

KZn₃F(BO₃)₂. Symmetry transformations used to generate equivalent atoms:

#1 x-1, y-1, z; #2 x, y-1, z; #3 x-1, y, z; #4 x+1, y, z; #5 x, y+1, z; #6 x+1, y+1, z; #7 -x+1, -y+2, -z+1; #8 -x+1, -y+2, z-1/2; #9 x-1, y, -z+1/2; #10 x, y, -z+1/2; #11 x, y+1, -z+1/2; #12 -x+2, -y+2, -z+1; #13 -y+1, x-y, z; #14 -y+1, x-y+1, z; #15 -y+2, x-y+1, z; #16 y, -x+y+1, -z+1; #17 -x+y, -x+1, z; #18 -x+y+1, -x+1, z; #19 -x+y, -x+2, z; #20 -x+y+1, -x+2, z; #21 x-y+1, x, -z+1; #22 -y+1, x-y+1, -z+1/2; #23 -x+y, -x+2, -z+1/2.

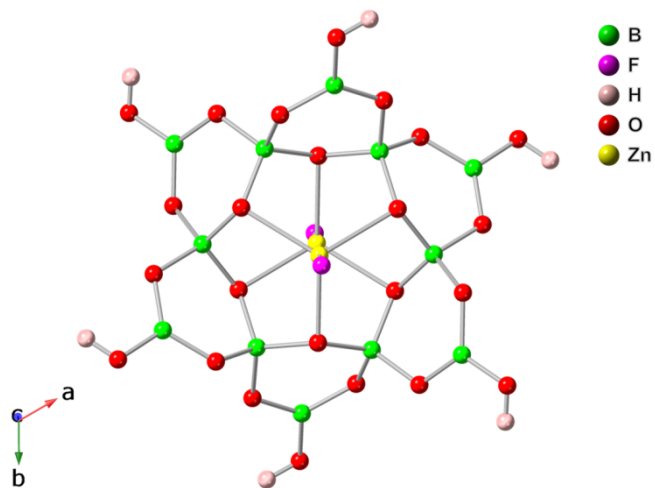


Figure S4: $[\text{ZnF}_2(\text{B}_{12}\text{O}_{24})\text{H}_6]^{6-}$ cluster structure of $\text{Na}_6\text{ZnF}_2(\text{B}_{12}\text{O}_{24})\text{H}_6$.

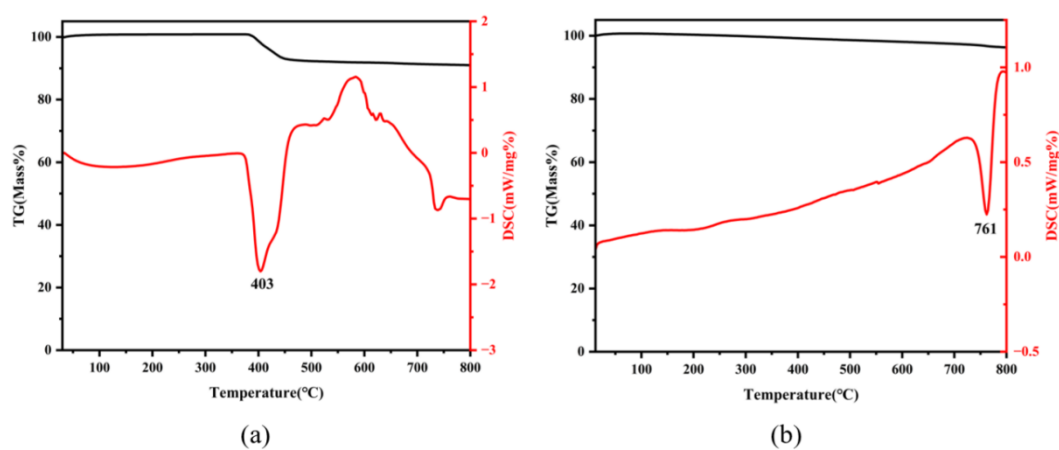


Figure S5: TG-DSC curves of $\text{Na}_6\text{ZnF}_2(\text{B}_{12}\text{O}_{24})\text{H}_6$ (a), $\text{KZn}_3\text{F}(\text{BO}_3)_2$ (b).

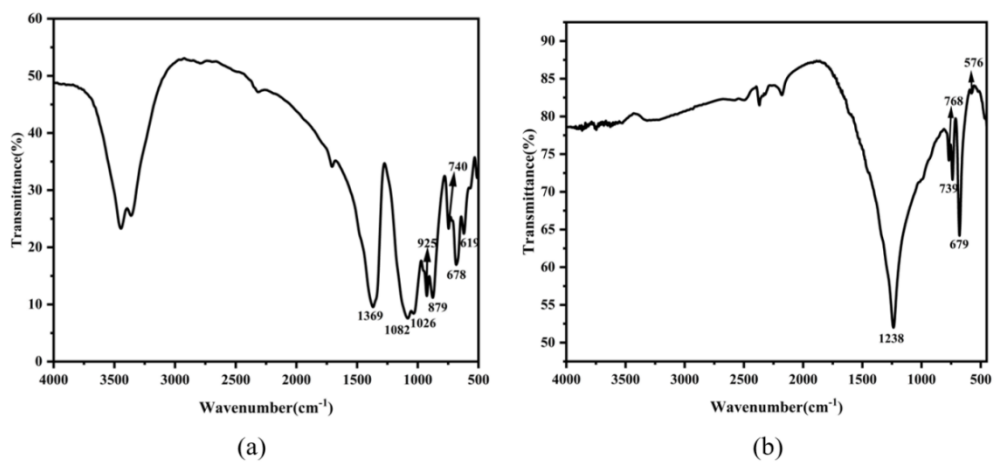


Figure S6: IR spectra of $\text{Na}_6\text{ZnF}_2(\text{B}_{12}\text{O}_{24})\text{H}_6$ (a), $\text{KZn}_3\text{F}(\text{BO}_3)_2$ (b).

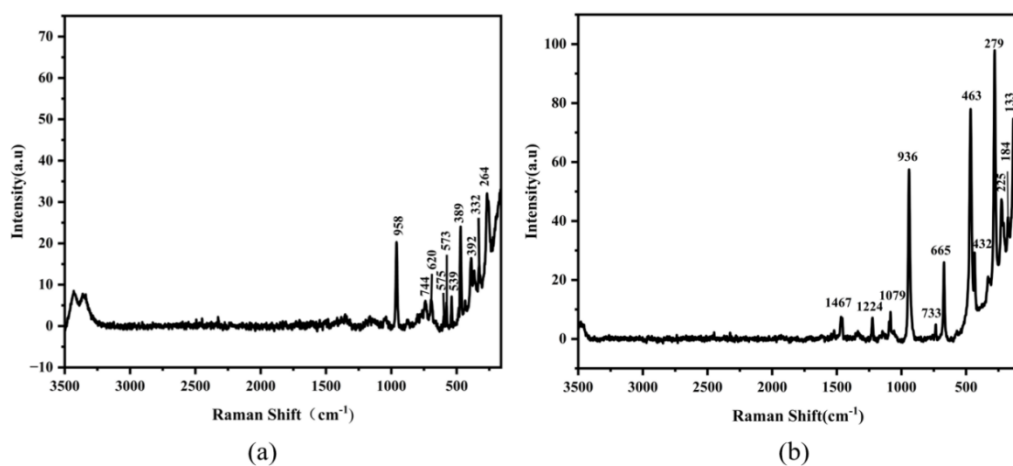


Figure S7: Raman spectra of $\text{Na}_6\text{ZnF}_2(\text{B}_{12}\text{O}_{24})\text{H}_6$ (a), $\text{KZn}_3\text{F}(\text{BO}_3)_2$ (b).

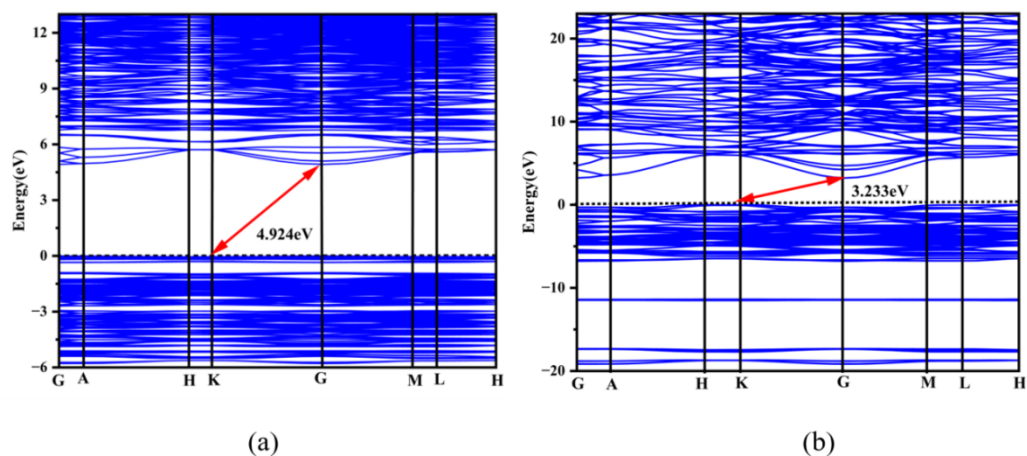


Figure S8: Calculated band gap of $\text{Na}_6\text{ZnF}_2(\text{B}_{12}\text{O}_{24})\text{H}_6$ (a), $\text{KZn}_3\text{F}(\text{BO}_3)_2$ (b).

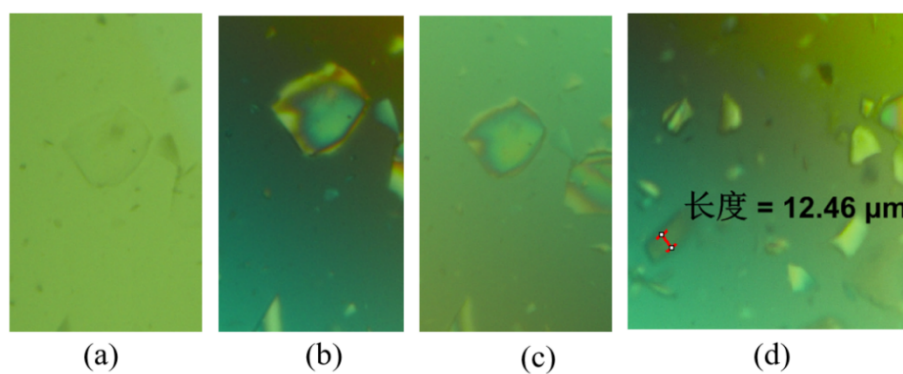


Figure S9: The crystal photographs of $\text{Na}_6\text{ZnF}_2(\text{B}_{12}\text{O}_{24})\text{H}_6$ in birefringence measurement. (a) Anomalous 0° crystal photograph; (b) Polarized 27.15° crystal photograph; (c) Polarized 33.25° crystal photograph; (d) Thickness photograph of the crystal.

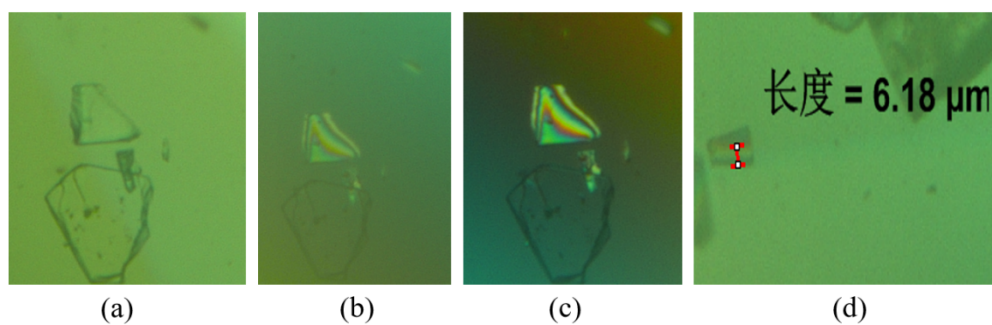


Figure S10: The crystal photographs of $\text{KZn}_3\text{F}(\text{BO}_3)_2$ in birefringence measurement. (a) Anomalous 0° crystal photograph; (b) Polarized 32.8° crystal photograph; (c) Polarized 27.1° crystal photograph; (d) Thickness photograph of the crystal.