"One Stone Two Birds" Design of Borates Featuring Edge-Sharing [BO_4] and Different B-O Configuration in One Structure Utilizing Covalent Tetrahedra

Haoran Wang,[ab#] Jiahao Jiao,[ab#] Abudukadi Tudi,[a] Shilie Pan,[a*] Min Zhang [a*]

[a] Research Center for Crystal Materials; State Key Laboratory of Functional Materials and Devices for Special Environmental Conditions, Xinjiang Key Laboratory of Functional Crystal Materials, Xinjiang Technical Institute of Physics and Chemistry, Chinese Academy and Science, Urumqi 830011, China.

[b] Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.

[#]These authors contributed equally to this work.

*Corresponding authors: slpan@ms.xjb.ac.cn, zhangmin@ms.xjb.ac.cn.

Table S1 Crystal data and structure refinements for $K_3Al_2B_{11}O_{21}$ and $K_3Al_2MoB_9O_{21}$.

Empirical formula	$K_3Al_2B_{11}O_{21}$	$K_3Al_2MoB_9O_{21}$
Formula weight	626.17	700.49
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions	a = 6.9336(8) Å	a = 7.0548(11) Å
	b = 22.240(3) Å	b = 11.9155(18) Å
	c = 13.3521(12) Å	c = 12.2046(18) Å
		α = 77.269(6)°
	β = 117.994(5) °	β = 78.861(7)°
		γ = 89.456(6)°
Volume (Å^3)	1818.0(4)	981.3(3)
Z	4	2
Calculated density (g·cm^{-3})	2.288	2.371
Absorption coefficient (mm^{-1})	0.960	1.498
F (000)	1224	676
Crystal size (mm^3)	0.13 × 0.087 × 0.08	0.271 × 0.149 × 0.102
Theta range for data collection	1.955 to 27.530 °	1.753 to 27.584 °
Limiting indices	$-9 \le h \le 9$,	$-9 \le h \le 9$
	$-28 \le k \le 26$,	$-15 \le k \le 15$
	$-16 \le l \le 17$	$-15 \le l \le 15$
Reflections collected / unique	16212 / 4166	37235 / 4530
	[R(int) = 0.0814]	[R(int) = 0.0564]
Completeness	99.9 %	99.9 %
Data / restraints / parameters	4166 / 0 / 334	4530 / 0 / 325
Goodness-of-fit on F^2	0.975	1.069
Final R indices [$Fo^2>2\sigma(Fo^2)$][a]	R_1 = 0.0488, wR_2 = 0.1086	R_1 = 0.0336, wR_2 = 0.0819
R indices (all data)[a]	R_1 = 0.0882, wR_2 = 0.1278	R_1 = 0.0406, wR_2 = 0.0848
Largest diff. peak and hole	0.672 and −0.582 e·Å^{-3}	1.314 and −0.718 e·Å^{-3}

[a] $R_1 = \Sigma||F_o| - |F||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$

Table S2 Atomic coordinates (× 10^4), equivalent isotropic displacement parameters (Å^2 × 10^3) and the bond valenc e sum (BVS) for $K_3Al_2B_{11}O_{21}$ and $K_3Al_2MoB_9O_{21}$

Atoms	*x*	*y*	*z*	$U_{(eq)}$	BVS
			$K_3Al_2B_{11}O_{21}$		
K(1)	6219(1)	-1070(1)	7519(1)	33(1)	1.03
K(2)	-3865(1)	-723(1)	2502(1)	33(1)	1.29
K(3)	-7161(2)	-2282(1)	1158(1)	43(1)	0.79
Al(1)	959(2)	924(1)	9079(1)	18(1)	2.94
Al(2)	-879(2)	-919(1)	5868(1)	20(1)	2.87
B(1)	1876(7)	-814(2)	9977(4)	21(1)	3.05
B(2)	4704(6)	-657(2)	9435(3)	18(1)	3.04
B(3)	997(6)	-331(2)	8180(4)	19(1)	3.06
B(4)	-1141(6)	254(2)	6855(4)	20(1)	3.06
B(5)	-4821(6)	600(2)	5593(4)	20(1)	3.06
B(6)	-2003(6)	736(2)	5036(4)	20(1)	3.07
B(7)	-2356(7)	-2027(2)	5307(4)	24(1)	3.03
B(8)	-5082(7)	-2725(2)	4108(4)	24(1)	3.03
B(9)	-2140(7)	-2471(2)	3637(4)	22(1)	3.04
B(10)	-1203(7)	-1948(2)	2280(4)	23(1)	3.06
B(11)	1036(7)	-2751(2)	3415(4)	23(1)	3.06
O(1)	1364(4)	-1023(1)	10768(2)	23(1)	2.00
O(2)	4074(4)	-797(1)	10249(2)	23(1)	2.15
O(3)	6799(4)	-715(1)	9667(2)	23(1)	1.98
O(4)	366(4)	-609(1)	8944(2)	23(1)	2.06
O(5)	3182(4)	-447(1)	8395(2)	22(1)	2.01
O(6)	503(4)	347(1)	8069(2)	21(1)	2.13
O(7)	-663(4)	-429(1)	6965(2)	20(1)	2.09
O(8)	-3322(4)	384(1)	6628(2)	22(1)	2.04
O(9)	-508(4)	527(1)	6088(2)	23(1)	2.03
O(10)	-6927(4)	648(1)	5357(2)	25(1)	2.04

O(11)	-4184(4)	764(1)	4797(2)	26(1)	2.08
O(12)	-1505(4)	910(1)	4239(2)	25(1)	1.99
O(13)	-1629(4)	-1618(1)	6148(2)	27(1)	1.88
O(14)	-4283(4)	-2346(1)	5018(2)	29(1)	2.02
O(15)	-1275(4)	-2128(1)	4696(2)	29(1)	1.93
O(16)	-4149(4)	-2794(1)	3429(2)	26(1)	2.06
O(17)	-2653(4)	-2057(1)	2682(2)	25(1)	1.99
O(18)	-455(4)	-2910(1)	3746(2)	26(1)	1.99
O(19)	-1560(4)	-1531(1)	1496(2)	29(1)	1.99
O(20)	730(4)	-2279(1)	2695(2)	28(1)	2.03
O(21)	3018(4)	-3038(1)	3882(2)	29(1)	2.00
		$K_3Al_2MoB_9O_{21}$			
K(1)	1674(1)	10146(1)	8395(1)	31(1)	1.04
K(2)	6611(1)	5052(1)	8474(1)	25(1)	1.21
K(3)	-2506(1)	849(1)	5666(1)	41(1)	1.17
Al(1)	1651(1)	6633(1)	8043(1)	14(1)	2.90
Al(2)	3310(1)	8114(1)	1521(1)	16(1)	2.91
Mo(1)	3141(1)	1961(1)	4868(1)	33(1)	6.13
B(1)	6104(4)	9547(2)	8420(3)	18(1)	3.05
B(2)	5189(4)	7633(2)	8298(3)	18(1)	3.04
B(3)	8590(4)	8188(2)	8051(3)	19(1)	3.04
B(4)	2130(5)	5861(3)	5853(3)	25(1)	3.10
B(5)	2766(5)	4619(3)	4526(3)	28(1)	3.08
B(6)	2488(5)	6644(3)	3805(3)	27(1)	3.07
B(7)	40(4)	7523(2)	812(3)	17(1)	3.04
B(8)	-3223(4)	6964(2)	783(3)	16(1)	3.05
B(9)	-596(4)	5670(2)	405(3)	15(1)	3.04
O(1)	5551(3)	10570(2)	8588(2)	23(1)	2.02
O(2)	4715(2)	8710(2)	8486(2)	22(1)	2.14

O(3)	3917(2)	6812(2)	8328(2)	21(1)	2.05
O(4)	8042(2)	9302(2)	8115(2)	23(1)	2.07
O(5)	7152(2)	7386(2)	8101(2)	23(1)	2.09
O(6)	10429(2)	7916(2)	7990(2)	22(1)	1.95
O(7)	1787(3)	6001(2)	6907(2)	32(1)	1.98
O(8)	2460(4)	4773(2)	5617(2)	35(1)	1.96
O(9)	2190(4)	6769(2)	4926(2)	36(1)	2.13
O(10)	2498(3)	7558(2)	2970(2)	33(1)	2.07
O(11)	2765(3)	5540(2)	3619(2)	30(1)	2.12
O(12)	3077(4)	3574(2)	4283(2)	42(1)	2.12
O(13)	3366(5)	1625(3)	6261(3)	69(1)	1.99
O(14)	1143(4)	1251(2)	4702(3)	67(1)	2.12
O(15)	5078(4)	1400(2)	4109(2)	47(1)	1.93
O(16)	1258(2)	8340(2)	902(2)	21(1)	1.97
O(17)	-1865(2)	7804(2)	774(2)	22(1)	2.05
O(18)	594(2)	6427(2)	760(2)	18(1)	2.03
O(19)	-225(2)	4420(1)	833(2)	15(1)	2.08
O(20)	-2610(2)	5916(2)	584(2)	17(1)	2.01
O(21)	-5104(2)	7172(2)	954(2)	21(1)	2.03

Table S3 Selected bond lengths (Å) and angles (°) for $K_3Al_2B_{11}O_{21}$.

K(1)-O(3)	2.816(3)	B(1)-O(1)	1.346(5)
K(1)-O(4)#1	2.793(3)	B(1)-O(2)	1.391(5)
K(1)-O(5)	3.167(3)	B(1)-O(4)	1.359(5)
K(1)-O(7)#1	2.958(3)	B(2)-O(2)	1.384(5)
K(1)-O(11)#2	2.814(3)	B(2)-O(3)	1.342(4)
K(1)-O(12)#2	3.019(3)	B(2)-O(5)	1.372(4)
K(1)-O(13)#1	3.104(3)	B(3)-O(4)	1.427(5)
K(1)-O(16)#3	2.867(3)	B(3)-O(5)	1.427(5)
K(1)-O(18)#3	3.100(3)	B(3)-O(6)	1.537(5)
K(2)-O(1)#4	3.092(3)	B(3)-O(7)	1.501(5)
K(2)-O(2)#4	2.661(3)	B(4)-O(6)	1.495(5)
K(2)-O(5)#2	2.994(3)	B(4)-O(7)	1.547(5)
K(2)-O(6)#2	2.896(3)	B(4)-O(8)	1.425(4)
K(2)-O(8)#5	2.802(3)	B(4)-O(9)	1.426(5)
K(2)-O(9)#2	2.751(2)	B(5)-O(8)	1.369(5)
K(2)-O(10)#5	2.651(3)	B(5)-O(10)	1.346(5)
K(2)-O(17)	3.060(3)	B(5)-O(11)	1.378(5)
K(2)-O(19)	3.098(3)	B(6)-O(9)	1.377(5)
K(3)-O(1)#4	2.942(3)	B(6)-O(11)	1.393(5)
K(3)-O(14)#7	3.136(3)	B(6)-O(12)	1.322(5)
K(3)-O(15)#6	2.906(3)	B(7)-O(13)	1.346(5)
K(3)-O(16)	2.985(3)	B(7)-O(14)	1.398(5)
K(3)-O(17)	2.862(3)	B(7)-O(15)	1.360(5)
K(3)-O(18)#6	2.978(3)	B(8)-O(14)	1.364(5)
K(3)-O(20)#8	3.028(3)	B(8)-O(16)	1.346(5)
K(3)-O(21)#6	3.179(3)	B(8)-O(21)#8	1.392(5)
		B(9)-O(15)	1.465(5)
Al(1)-O(1)#9	1.730(3)	B(9)-O(16)	1.473(5)
Al(1)-O(3)#10	1.730(3)	B(9)-O(17)	1.474(5)

Al(1)-O(6)	1.780(3)	B(9)-O(18)	1.476(5)
Al(1)-O(19)#2	1.698(3)	B(10)-O(17)	1.366(5)
Al(2)-O(7)	1.774(3)	B(10)-O(19)	1.333(5)
Al(2)-O(10)#5	1.738(3)	B(10)-O(20)	1.395(5)
Al(2)-O(12)#2	1.725(3)	B(11)-O(18)	1.349(5)
Al(2)-O(13)	1.734(3)	B(11)-O(20)	1.370(5)
		B(11)-O(21)	1.371(5)
O(1)#9-Al(1)-O(6)	109.73(13)	O(8)-B(5)-O(11)	120.4(3)
O(3)#10-Al(1)-O(1)#9	112.55(14)	O(10)-B(5)-O(8)	119.4(4)
O(3)#10-Al(1)-O(6)	107.39(13)	O(10)-B(5)-O(11)	120.2(3)
O(19)#2-Al(1)-O(1)#9	113.08(14)	O(9)-B(6)-O(11)	117.7(4)
O(19)#2-Al(1)-O(3)#10	110.55(14)	O(12)-B(6)-O(9)	124.3(4)
O(19)#2-Al(1)-O(6)	102.97(14)	O(12)-B(6)-O(11)	117.9(3)
O(10)#5-Al(2)-O(7)	105.13(13)	O(13)-B(7)-O(14)	120.6(4)
O(12)#2-Al(2)-O(7)	110.38(13)	O(13)-B(7)-O(15)	121.0(4)
O(12)#2-Al(2)-O(10)#5	111.55(14)	O(15)-B(7)-O(14)	118.4(4)
O(12)#2-Al(2)-O(13)	115.08(14)	O(14)-B(8)-O(21)#8	116.7(4)
O(13)-Al(2)-O(7)	106.92(14)	O(16)-B(8)-O(14)	123.2(4)
O(13)-Al(2)-O(10)#5	107.20(13)	O(16)-B(8)-O(21)#8	120.2(4)
O(1)-B(1)-O(2)	117.7(3)	O(15)-B(9)-O(16)	111.0(3)
O(1)-B(1)-O(4)	123.4(4)	O(15)-B(9)-O(17)	109.4(3)
O(4)-B(1)-O(2)	119.0(4)	O(15)-B(9)-O(18)	107.6(3)
O(3)-B(2)-O(2)	120.2(3)	O(16)-B(9)-O(17)	108.6(3)
O(3)-B(2)-O(5)	120.1(4)	O(16)-B(9)-O(18)	109.3(3)
O(5)-B(2)-O(2)	119.7(3)	O(17)-B(9)-O(18)	110.9(3)
O(4)-B(3)-O(6)	111.4(3)	O(17)-B(10)-O(20)	119.9(4)
O(4)-B(3)-O(7)	111.9(3)	O(19)-B(10)-O(17)	122.2(4)
O(5)-B(3)-O(4)	115.5(3)	O(19)-B(10)-O(20)	117.9(4)

O(5)-B(3)-O(6)	111.4(3)	O(18)-B(11)-O(20)	122.7(3)
O(5)-B(3)-O(7)	113.2(3)	O(18)-B(11)-O(21)	119.2(4)
O(7)-B(3)-O(6)	90.9(2)	O(20)-B(11)-O(21)	117.9(4)
O(6)-B(4)-O(7)	90.7(2)		
O(8)-B(4)-O(6)	113.3(3)		
O(8)-B(4)-O(7)	112.2(3)		
O(8)-B(4)-O(9)	114.5(3)		
O(9)-B(4)-O(6)	112.6(3)		
O(9)-B(4)-O(7)	111.3(3)		

Symmetry transformations used to generate equivalent atoms:

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

Table S4 Selected bond lengths (Å) and angles (°) for $K_3Al_2MoB_9O_{21}$.

K(1)-O(1)	2.8489(19)	Mo(1)-O(12)	1.901(2)
K(1)-O(2)	2.7344(19)	Mo(1)-O(13)	1.697(3)
K(1)-O(4)#2	2.8693(19)	Mo(1)-O(14)	1.718(3)
K(1)-O(6)#2	2.9782(19)	Mo(1)-O(15)	1.714(3)
K(1)-O(13)#4	2.852(3)		
K(1)-O(16)#3	2.8628(19)	B(1)-O(1)	1.322(3)
K(1)-O(16)#5	3.293(2)	B(1)-O(2)	1.383(3)
K(1)-O(17)#3	2.8576(19)	B(1)-O(4)	1.392(3)
K(2)-O(3)	2.8161(18)	B(2)-O(2)	1.380(3)
K(2)-O(5)	2.7355(19)	B(2)-O(3)	1.324(3)
K(2)-O(11)#7	2.751(2)	B(2)-O(5)	1.398(3)
K(2)-O(12)#7	3.368(3)	B(3)-O(4)	1.393(3)
K(2)-O(18)#7	2.7911(18)	B(3)-O(5)	1.384(3)
K(2)-O(19)#7	2.9513(18)	B(3)-O(6)	1.326(3)
K(2)-O(20)#6	2.9735(18)	B(4)-O(7)	1.309(4)
K(2)-O(20)#8	3.1175(19)	B(4)-O(8)	1.396(4)
K(2)-O(21)#6	2.7560(19)	B(4)-O(9)	1.377(4)
K(3)-O(4)#10	3.238(2)	B(5)-O(8)	1.360(4)
K(3)-O(9)#6	2.770(2)	B(5)-O(11)	1.376(4)
K(3)-O(10)#6	2.787(2)	B(5)-O(12)	1.348(4)
K(3)-O(13)#2	3.048(4)	B(6)-O(9)	1.385(4)
K(3)-O(14)	2.616(3)	B(6)-O(10)	1.317(4)
K(3)-O(14)#9	2.769(3)	B(6)-O(11)	1.389(4)
K(3)-O(15)#9	3.183(3)	B(7)-O(16)	1.341(3)
K(3)-O(15)#2	2.763(3)	B(7)-O(17)	1.389(3)
		B(7)-O(18)	1.370(3)
Al(1)-O(3)	1.7250(19)	B(8)-O(17)	1.389(3)
Al(1)-O(6)#2	1.7424(19)	B(8)-O(20)	1.375(3)
Al(1)-O(7)	1.705(2)	B(8)-O(21)	1.333(3)

Al(1)-O(19)#6	1.7889(19)	B(9)-O(18)	1.426(3)
Al(2)-O(1)#11	1.7365(19)	B(9)-O(19)#13	1.537(3)
Al(2)-O(10)	1.730(2)	B(9)-O(19)	1.505(3)
Al(2)-O(16)	1.7501(19)	B(9)-O(20)	1.433(3)
Al(2)-O(21)#12	1.7347(19)		
O(3)-Al(1)-O(6)#2	109.78(9)	O(5)-B(3)-O(4)	117.8(2)
O(3)-Al(1)-O(19)#6	110.79(9)	O(6)-B(3)-O(4)	120.0(2)
O(6)#2-Al(1)-O(19)#6	106.39(9)	O(6)-B(3)-O(5)	122.2(2)
O(7)-Al(1)-O(3)	110.81(11)	O(7)-B(4)-O(8)	121.2(3)
O(7)-Al(1)-O(6)#2	117.30(11)	O(7)-B(4)-O(9)	122.1(3)
O(7)-Al(1)-O(19)#6	101.30(10)	O(9)-B(4)-O(8)	116.7(3)
O(1)#11-Al(2)-O(16)	109.41(9)	O(8)-B(5)-O(11)	120.6(3)
O(10)-Al(2)-O(1)#11	105.98(11)	O(12)-B(5)-O(8)	122.1(3)
O(10)-Al(2)-O(16)	106.76(11)	O(12)-B(5)-O(11)	117.3(3)
O(10)-Al(2)-O(21)#12	109.44(11)	O(9)-B(6)-O(11)	117.5(3)
O(21)#12-Al(2)-O(1)#11	111.48(9)	O(10)-B(6)-O(9)	119.5(3)
O(21)#12-Al(2)-O(16)	113.39(9)	O(10)-B(6)-O(11)	122.9(3)
		O(16)-B(7)-O(17)	118.2(2)
O(13)-Mo(1)-O(12)	112.59(13)	O(16)-B(7)-O(18)	122.8(2)
O(13)-Mo(1)-O(14)	109.93(18)	O(18)-B(7)-O(17)	118.9(2)
O(13)-Mo(1)-O(15)	106.90(15)	O(20)-B(8)-O(17)	119.4(2)
O(14)-Mo(1)-O(12)	111.58(13)	O(21)-B(8)-O(17)	120.9(2)
O(15)-Mo(1)-O(12)	110.24(12)	O(21)-B(8)-O(20)	119.7(2)
O(15)-Mo(1)-O(14)	105.25(14)	O(18)-B(9)-O(19)#13	110.5(2)
		O(18)-B(9)-O(19)	113.0(2)
O(1)-B(1)-O(2)	119.2(2)	O(18)-B(9)-O(20)	114.8(2)
O(1)-B(1)-O(4)	122.2(2)	O(19)-B(9)-O(19)#13	90.49(18)
O(2)-B(1)-O(4)	118.6(2)	O(20)-B(9)-O(19)#13	112.6(2)

O(2)-B(2)-O(5)	117.3(2)	O(20)-B(9)-O(19)	113.0(2)
O(3)-B(2)-O(2)	124.5(2)		
O(3)-B(2)-O(5)	118.1(2)		

Symmetry transformations used to generate equivalent atoms:

#1 -x, -y+2, -z+2	#2 x-1, y, z	#3 -x, -y+2, -z+1	#4 x, y+1, z
#5 x, y, z+1	#6 -x, -y+1, -z+1	#7 -x+1, -y+1, -z+1	#8 x+1, y, z+1
#9 -x, -y, -z+1	#10 x-1, y-1, z	#11 -x+1, -y+2, -z+1	#12 x+1, y, z
#13 -x, -y+1, -z	#14 x+1, y+1, z	#15 x-1, y, z-1	#16 x, y-1, z
#17 x, y, z-1			

Table S5 Borates with edge-sharing [BO_4] tetrahedral structure. The compounds highlighted in red are the ones presented in this study.

Compound	Space Group	FBB	B-O Anionic Framework	A : B[a]	Covalent Tetrahedron	Synthesized Condition	Refrences
			High Pressure				
$RE_4B_6O_{15}$ (RE = Dy, Ho)	*C*2/*c*	B_6O_{18}	2D Monolayer	0.67	/	8.0 Gpa, 1000 ℃	[1]
α-$RE_2B_4O_9$ (RE = Eu, Gd, Tb, Dy, Sm, Ho, Y)	*C*2/*c*	$B_{20}O_{50}$	3D Network	0.50	/	7.5-12.3 Gpa, 1020-1150 ℃	[2]
$La_3B_6O_{13}(OH)$	$P2_1$	$B_{12}O_{32}(OH)_2$	2D Monolayer	0.50	/	6.0 GPa, 1400 ℃	[3]
HP-MB_2O_4 (M = Ni, Fe, Co)	*C*2/*c*	B_2O_6	2D Monolayer	0.50	/	6.5-8.0 GPa, 680-1030 ℃	[4]
γ-HfB_2O_5	$P2_1/c$	B_4O_{12}	2D Monolayer	0.50	/	114 GPa	[5]
$M_6B_{22}O_{39}·H_2O$ (M = Fe, Co)	$Pmn2_1$	$B_{11}O_{34}$	3D Network	0.27	/	6.0 GPa, 880 ℃	[6]
$Co_7B_{24}O_{42}(OH)_2·2H_2O$	*Pbam*	$B_{12}O_{32}(OH)_2$	3D Network	0.29	/	6.0 GPa, 880 ℃	[7]
HP-AB_3O_5 (A = K, NH_4, Rb, Tl, $Cs_{1-x}(H_3O)_x$)	*C*2/*c*	B_6O_{14}	3D Network	0.33	/	3.0-6.0 GPa, 600-1400 ℃	[8]
HP-CsB_5O_8	*P*nma	B_5O_{11}	3D Network	0.20	/	6.0 GPa, 900 ℃	[9]
$NaBSi_3O_8$	$P\bar{1}$	B_2O_6	0D Isolated [B_2O_6]	1.00	/	27.8 GPa	[10]
γ-BaB_2O_4	$P2_1/n$	B_8O_{18}	0D Isolated [B_8O_{18}]	0.50	/	3.0 GPa, 900 ℃	[11]
α-$Ba_3[B_{10}O_{17}(OH)_2]$	$P2_1/n$	$B_{20}O_{42}(OH)_4$	3D Network	0.30	/	1.0 GPa 500℃	[12]
			Atmosphere Pressure				
$KZnB_3O_6$	$P\bar{1}$	B_6O_{12}	0D Isolated [B_6O_{12}]	0.67	[ZnO_4]	750 ℃	[13]
$Ba_4Na_2Zn_4(B_3O_6)_2(B_{12}O_{24})$	$P\bar{1}$	B_3O_6 and $B_{12}O_{24}$	0D Isolated [B_3O_6] and [$B_{12}O_{24}$]	0.56	[ZnO_4]	750 ℃	[14]
$Li_4Na_2CsB_7O_{20}$	$P\bar{1}$	$B_{14}O_{28}$	0D Isolated [$B_{14}O_{28}$]	1.00	/	630 ℃	[15]

$BaAlBO_4$	$P2_1/c$	B_4O_{10}	0D Isolated $[B_4O_{10}]$	2.00	$[AlO_4]$	840 ℃	[16]
$Pb_{2.28}Ba_{1.72}B_{10}O_{19}$	$C2/c$	$B_{10}O_{24}$	3D Network	0.40	/	600 ℃	[17]
K_3SbBO_{13}	$C2/m$	B_2O_6	0D Isolated $[B_2O_6]$	4.00	/	1050 ℃	[18]
$Ba_6Zn_6(B_3O_6)_6(B_6O_{12})$	$P\bar{1}$	B_3O_6 and B_6O_{12}	0D Isolated $[B_3O_6]$ and $[B_6O_{12}]$	0.50	$[ZnO_4]$	800/880 ℃	[19]
$K_3Al_2B_{11}O_{21}$	$P2_1/c$	B_5O_{10} and B_6O_{12}	1D $^1_\infty[B_5O_9]$ Chain and 0D Isolated $[B_6O_{12}]$	0.45	$[AlO_4]$	600 ℃	This Work
$K_3Al_2MoB_9O_{21}$	$P\bar{1}$	B_3O_6 and B_6O_{12}	0D Isolated $[B_3O_6]$ and $[B_6O_{12}]$	0.67	$[AlO_4]$ and $[MoO_4]$	750 ℃	This Work
Vacuum							
β-CsB_9O_{14}	$P\bar{1}$	$B_{18}O_{34}$	Triple-layered	0.11	/	400 ℃	[20]

[a] "A : B" indicates the ratio of the number of B atoms to cations.

Table S6 Basic information of anhydrous borates containing two or more kinds of isolated B-O groups.

NO.	Chemical Formula [a]	Space Group	B-O Clusters	A : B [b]	Covalent Polyhedron	Ref
1	$Ho_{31}O_{27}(BO_3)_3(BO_4)_6$	$R\bar{3}$	$[BO_3]+[BO_4]$	3.44	/	[21]
2	$Ni_7U(BO_3)_2(BO_4)_2O_2$	*Pnnm*	$[BO_3]+[BO_4]$	2.00	/	[22]
3	$Al_8(BO_3)_4(B_2O_5)F_8$	$P4_2/nmc$	$[BO_3]+[B_2O_5]$	1.33	$[AlO_4F_2]$	[23]
4	$Ba_3Zn(BO_3)(B_2O_5)F$	$P2_1/c$	$[BO_3]+[B_2O_5]$	1.33	$[ZnO_4]$	[24]
5	$Ba_4Zn_2(BO_3)_2(B_2O_5)F_2$	$C2/c$	$[BO_3]+[B_2O_5]$	1.50	$[ZnO_4]$	[24]
6	$Ba_2Sc_2(BO_3)_2(B_2O_5)$	$C2/c$	$[BO_3]+[B_2O_5]$	1.00	/	[25]
7	$Sr_2Sc_2(BO_3)_2(B_2O_5)$	$P\bar{1}$	$[BO_3]+[B_2O_5]$	1.00	/	[25]
8	$Li_3Ba_4Sc_3(BO_3)_4(B_2O_5)_2$	$P\bar{1}$	$[BO_3]+[B_2O_5]$	1.25	/	[26]
9	$Ba_5(BO_3)_2(B_2O_5)$	$P2_12_12_1$	$[BO_3]+[B_2O_5]$	1.25	/	[27]
10	$Cu_{15}(BO_3)_6(B_2O_5)_2O_2$	$P\bar{1}$	$[BO_3]+[B_2O_5]$	1.50	/	[28]
11	$Cu_9Ti_2(BO_3)_2(B_2O_5)_2O_6$	$P\bar{1}$	$[BO_3]+[B_2O_5]$	1.83	$[TiO_6]$	[29]
12	$LiNa_5Be_{12}(BO_3)_6(B_2O_5)_3$	*Pc*	$[BO_3]+[B_2O_5]$	1.50	$[BeO_4]$	[30]
13	$Na_2Be_4(BO_3)_2(B_2O_5)$	*P*1	$[BO_3]+[B_2O_5]$	1.50	$[BeO_4]$	[30]
14	$Pb_8(BO_3)_2(B_2O_5)O_3$	*Ama*2	$[BO_3]+[B_2O_5]$	2.00	/	[31]
15	$Pb_3Ba_7(BO_3)_5(B_2O_5)F$	$Pmn2_1$	$[BO_3]+[B_2O_5]$	1.43	/	[32]
16	$Sr_2LiBe(BO_3)(B_2O_5)$	$P2_1/c$	$[BO_3]+[B_2O_5]$	1.33	$[BeO_4]$	[33]
17	$Cs_3Zn_6(BO_3)_3(B_3O_6)_2$	$Cmc2_1$	$[BO_3]+[B_3O_6]$	1.00	$[ZnO_4]$	[34]
18	$K_3Be_6(BO_3)_3(B_3O_6)_2$	$P2_1$	$[BO_3]+[B_3O_6]$	1.00	$[BeO_4]$	[35]
19	$Ca_3Be_6(BO_3)_2(B_3O_{10})F$	$P6_3/m$	$[BO_3]+[B_3O_{10}]$	1.80	$[BeO_4]$	[36]
20	$Ca_6Na_8Li_2Be_8(BO_3)_8(B_{12}O_{24})F_2$	$R\bar{3}$	$[BO_3] + [B_{12}O_{24}]$	1.20	$[BeO_4]$	[37]
21	$Cd_6Na_8Li_2Be_8(BO_3)_8(B_{12}O_{24})F_2$	$R\bar{3}$	$[BO_3] + [B_{12}O_{24}]$	1.20	$[BeO_4]$	[38]
22	$Sr_6Na_8Li_2Be_8(BO_3)_8(B_{12}O_{24})F_2$	$R\bar{3}$	$[BO_3] + [B_{12}O_{24}]$	1.20	$[BeO_4]$	[38]
23	$La_4(BO_3)(B_3O_8)F_2$	$P2_1/c$	$[BO_3] + [B_2O_5] + [B_3O_8]$	1.00	/	[39]

24	$Ba_6Al_4(BO_3)_2(B_6O_{13})(B_6O_{14})$	$P\bar{1}$	$[BO_3] + [B_6O_{13}] + [B_6O_{14}]$	0.71	$[AlO_4]$	[40]
25	$Ca_{10}Ge_{16}(BO_4)_2(B_2O_7)_2O_{29}$	*Pba*2	$[BO_4]+[B_2O_7]$	4.33	$[GeO_4] + [GeO_6]$	[41]
26	α-$Pb_2Ba_4Zn_4(B_2O_5)(B_6O_{13})_2$	*P*1	$[B_2O_5]+[B_6O_{13}]$	0.71	$[ZnO_4]$	[42]
27	β-$Pb_2Ba_4Zn_4(B_2O_5)(B_6O_{13})_2$	*Cc*	$[B_2O_5] + [B_6O_{13}]$	0.71	$[ZnO_4]$	[42]
28	γ-$Pb_2Ba_4Zn_4(B_2O_5)(B_6O_{13})_2$	$P3_2$	$[B_2O_5] + [B_6O_{13}]$	0.71	$[ZnO_4]$	[42]
29	$Ba_4Na_2Zn_4(B_3O_6)_2(B_{12}O_{24})$	$P\bar{1}$	$[B_3O_6] + [B_{12}O_{24}]$ (ES-$[BO_4]$)	0.56	$[ZnO_4]$	[14]
30	$Ba_6Zn_6(B_3O_6)_6(B_6O_{12})$	$P\bar{1}$	$[B_3O_6] + [B_6O_{12}]$ (ES-$[BO_4]$)	0.50	$[ZnO_4]$	[19]
31	$K_3Al_2MoO_3(B_3O_6)(B_6O_{12})$	$P\bar{1}$	$[B_3O_6] + [B_6O_{12}]$ (ES-$[BO_4]$)	0.67	$[AlO_4] + [MoO_4]$	This work
32	$Rb_{18}Mg_6(B_5O_{10})_3(B_7O_{14})_2F$	*C*2/*c*	$[B_5O_{10}] + [B_7O_{14}]$	0.83	/	[43]

[a] The compounds on either side of the " / " sign are the same one in the chemical formula column.

[b] "A : B" indicates the ratio of the number of B atoms to cations.

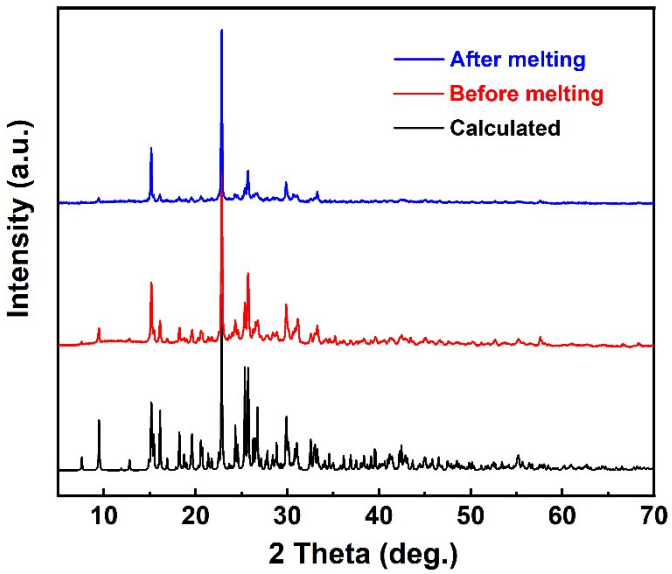

Figure S1 Experimental and calculated powder X-ray diffraction patterns of $K_3Al_2MoB_9O_{21}$

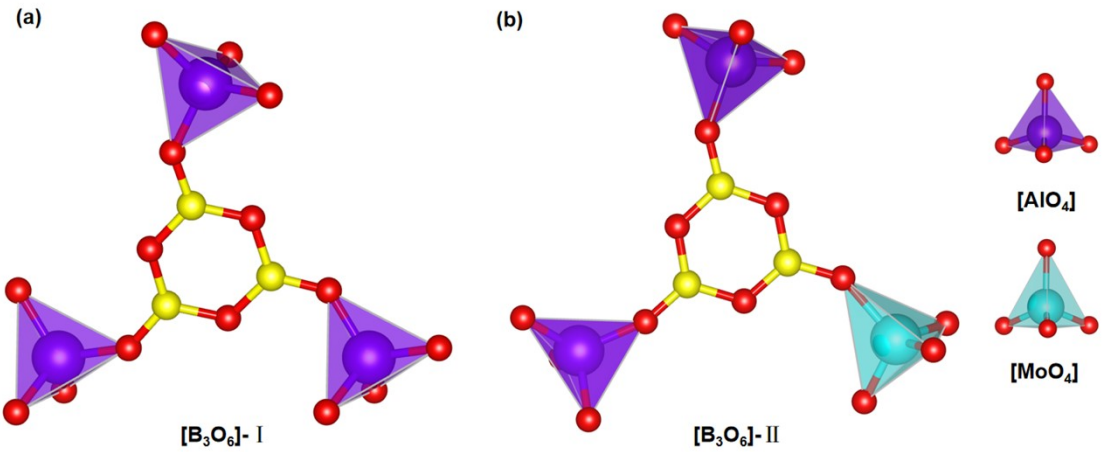

Figure S2 The structures of (a) $[B_3O_6]$-I and (b) $[B_3O_6]$-II.

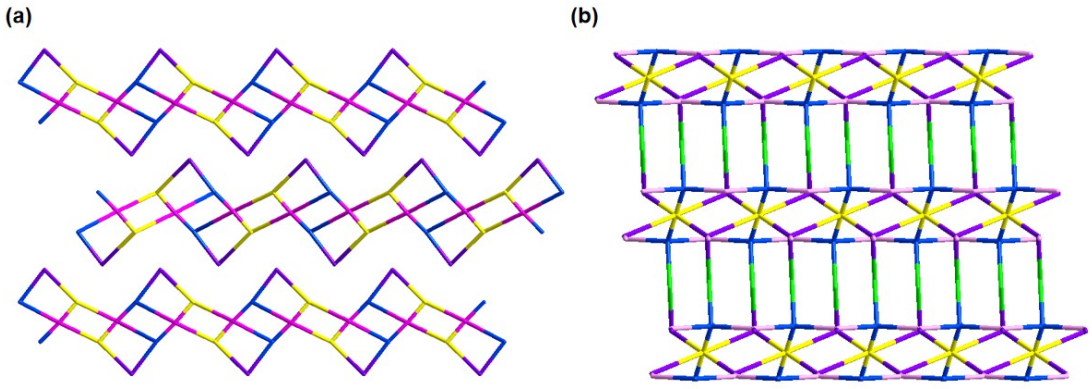

Figure S3 The topological structure of (a) $K_3Al_2B_{11}O_{21}$ where the $[Al_2B_{11}O_{21}]$ are regarded as four-nodal net, (b) $K_3Al_2MoB_9O_{21}$ where the $[Al_2B_9O_{21}]$ are regarded as five-nodal net.

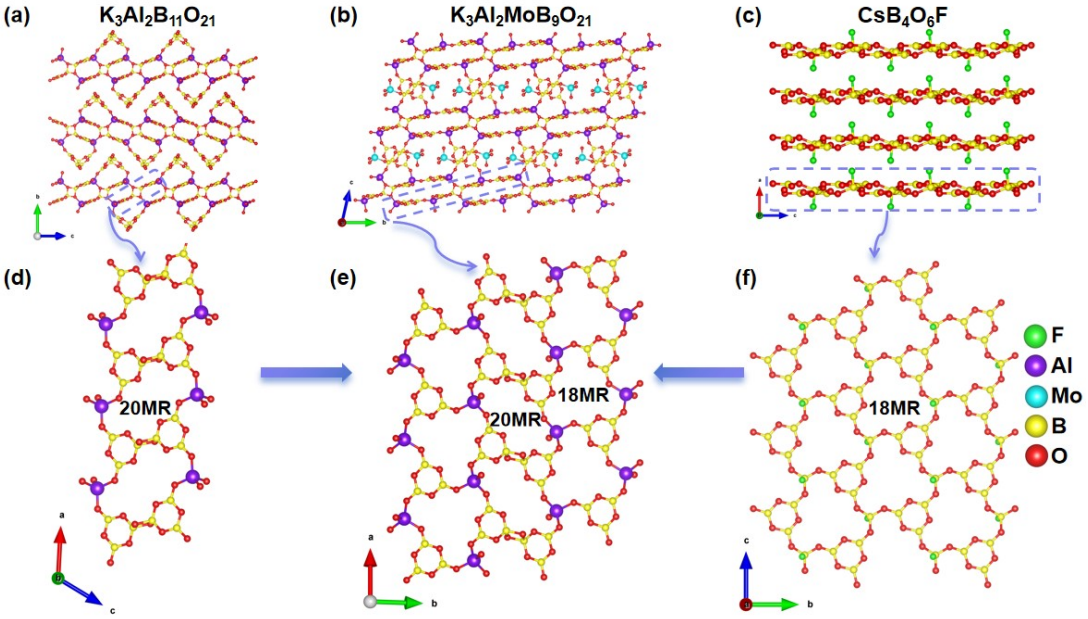

Figure S4 The anionic framework of (a) $K_3Al_2B_{11}O_{21}$, (b) $K_3Al_2MoB_9O_{21}$, (c) CsB_4O_6F and multivariate rings in (d) $K_3Al_2B_{11}O_{21}$, (e) $K_3Al_2MoB_9O_{21}$, (f) CsB_4O_6F.

Figure S5 The replacement node in FBB contains B-OH groups.

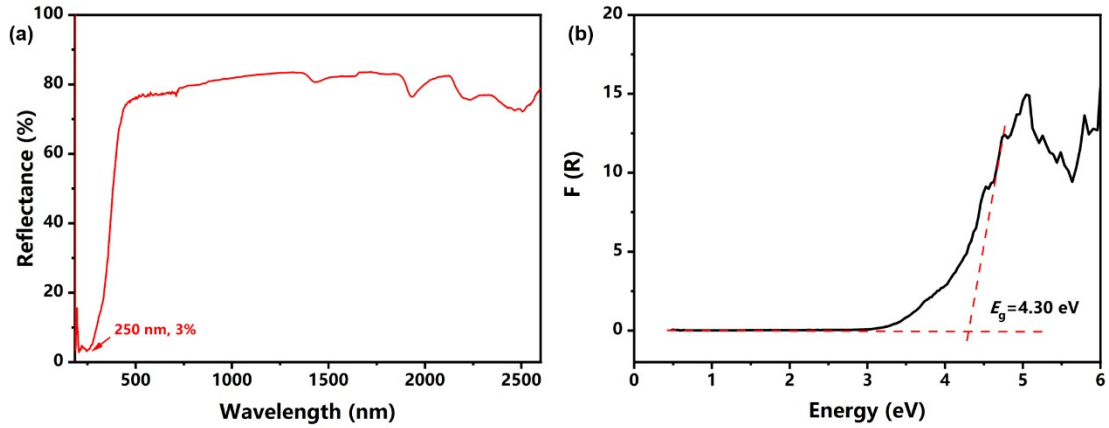

Figure S6 (a) UV-Vis-NIR diffuse reflectance spectrum and (b) the experimental bandgap of $K_3Al_2MoB_9O_{21}$.

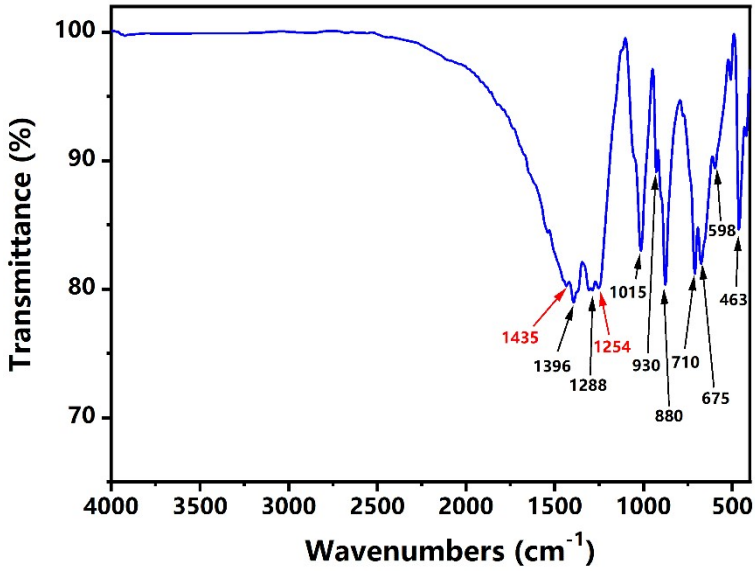

Figure S7 Infrared spectrum of $K_3Al_2MoB_9O_{21}$.

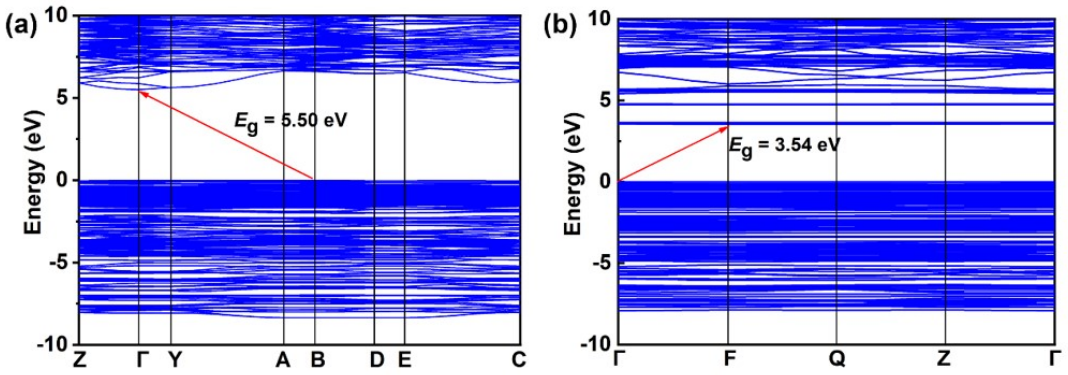

Figure S8 Band structures of (a) $K_3Al_2B_{11}O_{21}$, (b) $K_3Al_2MoB_9O_{21}$.

References

1. (a) H. Hubertz and V.Benjamin, *J. Am. Chem. Soc*., 2002, **124**, 9376; (b) H. Huppertz, *Z. Naturforsch*., 2003, **58**, 278-290.
2. (a) H. Emme and H. Huppertz, *Chem. Eur. J*., 2003, **9**, 3623-3633; (b) H. Emme and H. Huppertz, *Acta. Crystallogr*., 2005, **61**, i29-i31; (*c*) M. Schmitt and H. Huppertz, *Z. Naturforsch*., 2017, **72**, 977-982.
3. B. Fuchs, G. Heymann, X. Wang, A. Tudi, L. Bayarjargal, R. Siegel, A. Schmutzler, J. Senker, M. Joachim, A. Saxer, Z. Yang, S. Pan and H. Huppertz, *Chem. Eur. J*., 2020, **26**, 6851-6861.
4. (a) J. Knyrim, F. Roeßner, S. Jakob, D. Johrendt, I. Kinski, R. Glaum and H. Huppertz, *Angew. Chem. Int. Ed*., 2007, **46**, 9097-9100; (b) S. Neumair, R. Glaum and H. Huppertz, *Z. Naturforsch*., 2009, **64b**, 883-890; (c) S. Neumair, R. Glaum and H. Huppertz, *Z. Naturforsch*., 2010, **65b**, 1311-1317.
5. A. Pakhomova, B. Fuchs, L. Dubrovinsky, N. Dubrovinskaia and H. Huppertz, *Chem. Eur. J*., 2021, **27**, 6007-6014.
6. S. Neumair, J. Knyrim, O. Oeckler, R. Glaum, R. Kaindl, R. Stalder and H. Huppertz, *Chem. Eur. J*., 2010, **16**, 13659-13670.
7. S. Neumair, R. Kaindl and H. Huppertz, *J. Solid. State. Chem*., 2012, **185**, 1-9.
8. (a) S. Neumair, S. Vanicek, R. Kaindl, D. Többens, C. Martineau, F. Taulelle, J. Senker and H. Huppertz, *Eur. J. Inorg. Chem*., 2011, **42**, 4147-4152; (b) G. Sohr, D. Wilhelm, D. Vitzthum, M. Schmitt and H. Huppertz, *Z. Anorg. Allg. Chem*., 2014, **640**, 2753-2758; (c) G. Sohr, S. Neumair and H. Huppertz, *Z. Naturforsch*., 2012, **67b**, 1197-1204; (d) G. Sohr, L. Perfler and H. Huppertz, *Z. Naturforsch*., 2014, **69b**, 1260-1268; (e) G. Sohr, S. Neumair, G. Heymann, K. Wurst, J. Günne and H. Huppertz, *Chem. Eur. J*., 2014, **20**, 4316-4323.
9. G. Sohr, D.Többens, J. Günne and H. Huppertz, *Chem. Eur. J.*, 2014, **20**, 17059-17067.
10. L. Gorelova, A. Pakhomova, G. Aprilis, Y. Yin, D. Laniel, B. Winkler, S. Krivovichev, I. Pekov, N. Dubrovinskaia and L. Dubrovinsky, *Inorg. Chem. Front*., 2022, **9**, 1735-1742.
11. T. Bekker, I. Podborodnikov, N. Sagatov, A. Shatskiy, S. Rashchenko, D. Sagatova, A. Davydov and K. Litasov, *Inorg.. Chem*., 2022, **61**, 2340-2350.
12. I. Jen, Y.Lee, C.Tsai and K. Lii, *Inorg. Chem*., 2019, **58**, 4085-4088.
13. S. Jin, G. Cai, W. Wang, M. He, S. Wang and X. Chen. *Angew. Chem. Int. Ed*., 2010, **49**, 4967-4970
14. X. Chen, Y. Chen, C. Sun, X. Chang and W. Xiao. *J. Alloys. Compd*., 2013, **568**, 60-67.
15. M. Mutailipu, M. Zhang, H. Li, X. Fan, Z. Yang, S. Jin, G. Wang and S. Pan, *Chem. Commun*., 2019, **55**, 1295-1298.
16. F. Guo, J. Han, S. Cheng, S. Yu, Z. Yang and S. Pan, *Inorg. Chem*., 2019, **58**, 8237-8244.
17. S. Guo, W. Zhang, R. Yang, M. Zhang, Z. Yang and S. Pan, *Inorg. Chem. Front*., 2021, **8**, 3716-3722.

18. E. Quarez, E. Gautron, M. Paris, D. Gajan and J. Mevellec. *Inorg*. *Chem*., 2021, **60**, 2406-2413.
19. (a) J. Han, K. Liu, L. Chen, F. Li, Z. Yang, F. Zhang, S. Pan and M. Mutailipu. *Chem*. *Eur*. *J*., 2023, **29**, e202203000; (b) W. Xie, Z. Fang. and J. Mao, *Inorg*. *Chem*., 2022, **61**, 18260-18266.
20. S. Han, C. Huang, A. Tudi, S. Hu, Z. Yang and S. Pan, *Chem*. *Eur*. *J*., 2019, **25**, 11614-11619.
21. S. Hering, A. Haberer, R. Kaindl and H. Huppertz. *J*. *Solid State Sci*., 2010, **12**, 1993-2002.
22. M. Gasperin. *Acta*. *Crystallogr*., 1989. **C45**, 981-983.
23. Y. Wang, J. Han, J. Huang, Z. Yang and S. Pan, *Inorg*. *Chem*., 2020, **59**, 810-817.
24. M. Mutailipu, X. Su, M. Zhang, Z. Yang and S. Pan, *Inorg*. *Chem*. *Front*., 2017, **4**, 281-288.
25. P. Thompson, J. Huang, R. Smith and D. Keszler, *J*. *Solid State Chem*., 1991, **95**, 126-135.
26. X. Meng, M. Xia and R. Li, *New*. *J*. *Chem*., 2019, **43**, 11469-11472.
27. N. Furmanova, B. Maksimov, V. Molchanov, A. Kokh, N. Kononova and P. Fedorov, *Crystallogr*. *Rep*., 2006, **51**, 219-224.
28. B. Behm, *Acta*. *Crystallogr*., 1982, **B38**, 2781-2784.
29. J. Schaefer and K. Bluhm, *Z*. *Anorn*. *Alln*. *Chem*., 1994, **620**, 1583-1588.
30. H. Huang, L. Liu, S. Jin, W. Yao, Y. Zhang and C. Chen, *J*. *Am*. *Chem*. *Soc*., 2013, **135**, 18319-18322.
31. H. Yu, S. Pan, H. Wu, W. Zhao, F. Zhang, H. Li and Z. Yang, *J*. *Mater*. *Chem*., 2012, **22**, 2105-2110.
32. W. Zhang, W. Jin, S. Han, Z. Yang and S. Pan, *Scripta*. *Mater*., 2021, **194**, 113700.
33. N. Yu and N. Ye. *Acta*. *Crystallogr*., 2012, **68**, i32-i32.
34. S. Zhao, J. Zhang, S. Zhang, Z. Sun, Z. Lin, Y. Wu, M. Hong and J. Luo, *Inorg*. *Chem*., 2014, **53**, 2521-2527.
35. S. Wang, N. Ye, W. Li and D. Zhao, *J*. *Am*. *Chem*. *Soc*., 2010, **132**, 8779-8786.
36. W. Yao, T. Xu, X. Jiang, H. Huang, X. Wang, Z. Lin and C. Chen, *Dalton Trans*., 2014, **43**, 9998-10004.
37. S. Luo, W. Yao, P. Gong, J. Yao, Z. Lin and C. Chen, *Inorg*. *Chem*., 2014, **53**, 8197-8199.
38. X. Wang, L. Liu, M. Xia, X. Wang and C. Chen, *Chinese J*. *Struct*. *Chem*., 2015, **34**, 1617-1625.
39. A. Haberer, R. Kaindl, O. Oeckler and H. Huppertz, *J*. *Solid State Chem*., 2010, **183**, 1970-1979.
40. X. Chen, J. Yue, X. Chang and W. Xiao. *J*. *Solid State Chem*., 2017, **245**, 174-183.
41. X. Xu, C. Hu, F. Kong, J. Zhang and J. Mao, *Inorg*. *Chem*., 2011, **50**, 8861-8868.
42. H. Yu, H. Wu, Q. Jing, Z. Yang, P. Halasyamani and S. Pan, *Chem*. *Mater*., 2015, **27**, 4779-4788.
43. Z. Wang, M. Zhang, X. Su, S. Pan, Z. Yang, H. Zhang and L. Liu, *Chemistry*, 2015, **21**, 1414-1419.