Supporting Information.

Thermodynamic properties and structure of the gaseous $BMoO_4$

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Table S1. Equilibrium data for the gas-phase reaction (6).

Table S2. Thermodynamic functions of $BMoO_4$, BWO_4, BPO_3 and BPO_4 molecules

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Table S1 Equilibrium Data for the Gas Phase Reaction (7) for the $B_2O_3 - Ga_2O - Mo$ System.

T, K	p_i, atm				$-\Delta_r H^0$, kJ
	B_2O_3 $\times 10^5$	MoO_3 $\times 10^6$	MoO_2 $\times 10^6$	$BMoO_4$ $\times 10^6$	
1564	3.9	1.7	0.5	1.3	276.0
1566	3.8	1.3	0.7	1.2	273.7
1561	3.3	1.8	0.9	1.5	273.0
1568	3.1	0.9	0.5	1.0	281.1
1566	2.2	1.0	0.5	0.6	270.5
1571	2.2	0.5	0.3	0.6	287.1
1588	1.9	1.1	0.7	1.3	290.6
1588	1.8	0.8	0.4	0.4	271.8
1521	8.6	1.7	8.1	9.8	274.9
1524	7.9	4.3	5.8	9.0	266.8
1537	9.0	4.1	7.6	10.7	268.8
1539	8.7	4.1	7.0	8.3	264.1
1539	6.2	3.7	5.8	7.4	269.2
1533	6.2	3.0	4.6	4.9	263.4
1529	1.9	2.4	3.8	4.7	282.0
1547	0.9	3.6	6.5	5.0	284.1
1547	0.9	1.7	5.3	3.5	287.2
1544	0.4	1.7	4.1	1.5	278.7
				Average value:	275.7±8.2

Table S2. Thermodynamic functions: free energy function Φ°, entropy S°, enthalpy increment H(T)-H(0 K)·and heat capacity C_p°,of gaseous $BMoO_4$, BWO_4, BPO_3 and BPO_4 at selected temperatures in the temperature range 298.15 K to 2500 K

T	$\Phi°_m(T)$[a]	$S°_m(T)$	H(T)-H(0 K)·	$C_{p,m}°(T)$
K	$J·K^{-1}·mol^{-1}$	$J·K^{-1}·mol^{-1}$	$J·mol^{-1}$	$J·K^{-1}·mol^{-1}$
		$BMoO_4$		
298.15	299.6	368.7	20600.6	69.1
1000	401.6	501.2	99562.9	99.6
1100	411.2	513.0	111965.2	101.8
1200	420.1	523.9	124493.4	103.7
1300	428.5	534.0	137123.9	105.5
1400	436.4	543.4	149838.5	107.0
1500	443.8	552.2	162622.8	108.4
1600	450.9	560.5	175465.5	109.7
1700	457.5	568.3	188357.4	110.8
1800	463.9	575.7	201291.3	111.8
1900	470.0	582.7	214261.2	112.8
2000	475.8	589.4	227262.1	113.6
2100	481.3	595.8	240290.0	114.4
2200	486.7	601.8	253341.5	115.2
2300	491.8	607.7	266413.6	115.8
2400	496.8	613.2	279504.0	116.5
2500	501.5	618.6	292610.6	117.0
		BWO_4		
298.15	306.4	376.2	20796.8	69.8
1000	408.9	508.8	99842.1	99.8
1100	418.5	520.6	112245.6	102.0
1200	427.5	531.5	124774.5	104.0
1300	435.9	541.6	137405.4	105.7
1400	443.8	551.0	150120.2	107.2
1500	451.2	559.8	162904.5	108.6
1600	458.3	568.1	175747.1	109.8
1700	465.0	575.9	188639.0	111.0
1800	471.4	583.3	201572.8	112.0

1900	477.4	590.4	214542.5	112.9
2000	483.2	597.0	227543.3	113.8
2100	488.8	603.4	240571.0	114.6
2200	494.2	609.4	253622.2	115.3
2300	499.3	615.3	266694.2	116.0
2400	504.3	620.8	279784.4	116.6
2500	509.0	626.2	292890.8	117.2
		BPO_4		
298.15	262.0	322.2	17957.6	60.2
1000	355.1	449.4	94230.8	94.2
1100	364.2	461.0	106462.2	96.8
1200	372.8	471.8	118843.8	99.0
1300	380.8	481.8	131347.5	101.0
1400	388.3	491.1	143951.4	102.8
1500	395.5	499.9	156638.3	104.4
1600	402.3	508.1	169394.8	105.9
1700	408.7	515.9	182209.9	107.2
1800	414.9	523.3	195075.0	108.4
1900	420.8	530.2	207982.8	109.5
2000	426.4	536.9	220927.5	110.5
2100	431.8	543.2	233904.3	111.4
2200	437.0	549.3	246909.1	112.2
2300	442.0	555.0	259938.5	113.0
2400	446.9	560.6	272989.6	113.8
2500	451.5	565.9	286059.9	114.4
		BPO_3		
298.15	259.0	314.0	16417.4	55.1
1000	340.0	419.4	79384.3	79.4
1100	347.7	428.9	89365.8	81.2
1200	354.8	437.7	99461.6	82.9
1300	361.5	445.8	109650.7	84.4
1400	367.8	453.5	119916.7	85.7
1500	373.8	460.6	130246.6	86.8
1600	379.4	467.3	140630.1	87.9
1700	384.7	473.6	151058.9	88.9

1800	389.9	479.6	161526.3	89.7
1900	394.7	485.3	172026.9	90.5
2000	399.4	490.7	182556.1	91.3
2100	403.9	495.8	193110.2	92.0
2200	408.2	500.7	203686.0	92.6
2300	412.3	505.4	214280.9	93.2
2400	416.3	510.0	224892.8	93.7
2500	420.1	514.3	235519.6	94.2

[a] $\Phi^\circ_m(T) = \{G^\circ_m(T) - H^\circ_m(0\ K)\}/T$.

Table S3 Equilibrium geometry parameters and vibrational frequencies of two isomers of $BMoO_4$ calculated at the B3LYP level

Geometric parameters (Å, deg)	Structure I (C_{2v})	Structure II (C_s)
r(Mo-O_2)	2.217	1.921
r(Mo-O_4)	1.685	1.682
r(B-O_1)	1.268	1.212
r(B-O_2)	1.268	1.311
∠(O_1-Mo-O_2)	65.7	-
∠(O_3-Mo-O_4)	113.4	110.9
∠(O_1-B-O_2)	143.1	179.1
∠(B-O_2-Mo)	75.6	164.3
	122 (B_2)	27 (A")
	145 (A_2)	58 (A')
	150 (B_1)	157 (A')
	280 (B_2)	192 (A")
	283 (A_1)	322 (A')
Frequencies (cm^{-1})	382 (A_1)	453 (A')
	542 (B_1)	511 (A")
	703 (A_1)	531 (A')
	979 (B_1)	988 (A")
	1030 (A_1)	1032 (A')
	1200 (A_1)	1156 (A')
	1815 (B_2)	2059 (A')

Table S4 Equilibrium geometry parameters and vibrational frequencies of BWO_4 isomers calculated at the B3LYP level

Geometric parameters (Å, deg)	Structure I (C_{2v})	Structure II (C_s)	Structure III (C_{3v})
r(W-O_2)	2.208	1.925	2.077
r(W-O_4)	1.707	1.706	1.739
r(B-O_1)	1.273	1.210	-
r(B-O_2)	1.273	1.313	1.224
∠(O_1-W-O_2)	65.5	-	109.4
∠(O_3-W-O_4)	111.0	110.4	109.5
∠(O_1-B-O_2)	140.0	179.3	-
∠(B-O_2-W)	77.2	166.7	180.0
Frequencies (cm^{-1})	123 (B_2)	27 (A")	74 (E)
	141 (A_2)	55 (A')	191 (E)
	144 (B_1)	138 (A')	250 (A_1)
	272 (B_2)	186 (A")	308 (E)
	274 (A_1)	317 (A')	349 (A_1)
	353 (A_1)	431 (A')	643 (E)
	542 (B_1)	509 (A")	990 (A_1)
	693 (A_1)	525 (A')	1674 (A_1)
	981 (B_1)	985 (A")	
	1033 (A_1)	1032 (A')	
	1187 (A_1)	1165 (A")	
	1777 (B_2)	2068 (A')	

Table S5 Equilibrium geometry parameters and vibrational frequencies of BPO_4 singlet and triplet structures calculated at the B3LYP level

Geometric parameters (Å, deg)	Structure I singlet (C_s)	Structure I triplet (C_{2v})	Structure II triplet (C_s)
r(P-O_2)	1.595	1.632	1.628
r(P-O_4)	1.447	1.500	1.522
r(B-O_1)	1.202	1.392	1.206
r(B-O_2)	1.338	1.392	1.326
∠(O_1-P-O_2)	-	84.2	-
∠(O_3-P-O_4)	135.6	105.4	103.1
∠(O_1-B-O_2)	176.4	103.6	178.9
∠(B-O_2-P)	131.6	86.1	136.2
Frequencies (cm^{-1})	84 (A")	235 (B_1)	21 (A")
	98 (A')	249 (A_2)	106 (A')
	375 (A')	349 (A_1)	268 (A")
	412 (A')	398 (B_2)	314 (A')
	414 (A")	486 (B_1)	408 (A')
	503 (A")	635 (B_2)	489 (A")
	533 (A')	673 (A_1)	504 (A')
	724 (A')	905 (B_1)	658 (A')
	1115 (A')	915 (A_1)	792 (A")
	1130 (A')	1137 (A_1)	1049 (A')
	1478 (A')	1146 (B_2)	1128 (A')
	2088 (A')	1209 (A_1)	2078 (A')

Table S6 Equilibrium geometry parameters and vibrational frequencies of BPO_3 singlet isomers calculated at the B3LYP level

Geometric parameters (Å, deg)	Structure I (C_{3v})	Structure II (C_{2v})	Structure III (C_s)	Structure IV (C_s)	Structure V (C_{2v})
R(P-B)	1.762	1.900	-	-	2.186
r(P-O_1)	1.723	-	-	1.602	-
r(B-O_1)	1.433	1.195	1.208	1.314	1.221
R(B-O_2)	-	-	1.324	-	1.570
r(P-O_2)	-	1.453	1.661	1.448	1.550
R(P-O_3)	-	-	1.456	1.447	1.550
∠(O_2-P-O_3)	102.1	135.4	107.6	135.6	91.8
∠(B-O_1-P)	67.1	-	-	150.9	-
∠(B-O_2-P)	-	-	-	-	88.9
Frequencies (cm^{-1})	236 (E)	137 (B_2)	75 (A")	46 (A")	203 (B_1)
	646 (A_1)	231 (B_1)	102 (A')	99 (A')	252 (B_2)
	647 (E)	374 (A_1)	357 (A')	404 (A')	388 (B_2)
	957 (A_1)	415 (B_1)	504 (A')	409 (A")	551 (A_1)
	1014 (E)	418 (B_2)	512 (A")	429 (A')	620 (B_1)
	1213 (A_1)	577 (A_1)	649 (A')	735 (A')	689 (A_1)
		1159 (A_1)	1101 (A')	1175 (A')	1052 (B_2)
		1470 (B_2)	1312 (A')	1364 (A')	1067 (A_1)
		2028 (A_1)	2068 (A')	1480 (A')	1832 (A_1)