substance: boron compounds with group VI elements
property: properties of boron-oxygen compounds: B_6O, $B_{12}O_2$, B_7O

Structure, chemical bond

Kinetics of the formation of boron suboxide (B_6O) [87U].

Preparation by hot pressing and reaction study of $B_{12}O_2$ [86B].

Preparation by the reaction of other oxides with amorphous boron powders [93O].

For charges see [94B1, 90K].

There is no bond between the two oxygen atoms [94B1, 91H, 91L1].

X-ray emission used to calculate the O-O distance in [90K].

Rhombohedral lattice constant, angle and interatomic bond lengths obtained by ab initio calculations compared with experiment in [91L1].

Synthesis and stucture of non-stoichiometric B_6O [97O].

Nucleation and growth of icosahedral boron suboxide clusters at high pressure. The stoichiometry of $B_6O_{1-\delta}$ synthesized at high pressures lies closer to the nominal composition ($\delta = 0$) than materials obtained at atmospheric pressure (synthesis at T = 1700...1800 °C at pressures between 4 and approximately 5.5 GPa) [97M, 99M].

Icosahedral packing of B_{12} icosahedra in boron suboxide (B_6O) in [98H2].

High-pressure, high-temperature synthesis and characterization of boron suboxide [96H, 98H1].

Scanning electron micrographs, low-magnification and high-resolution TEM pictures in [97G2, 97H, 98H2, 99M]

α-rhombohedral boron structure group

Space group: $D_{3d}^5 - R\bar{3}m$.

lattice parameters and interatomic distances
(in Å)

B_6O

a	5.3862(3)	prepared by hot pressing	91B
	5.366(1)	prepared by reaction sintering	
c	12.319(1)	prepared by hot pressing	
	12.331(3)	prepared by reaction sintering	
V	309.51 $Å^3$	prepared by hot pressing	
	307.45 $Å^3$	prepared by reaction sintering	
a	5.374(2)	prepared by oxidation of	91H
c	12.331(3)	amorphous boron	
V	308.4(3) $Å^3$		
a	5.367(1)	prepared by oxidizing B with ZnO	93K
c	12.328(2)		

Oxygen site occupancy 0.76(6) [93K].

B_6O_{1-x}

a	5.3824(4)	T_{prep} = 1450 K	$B_6O_{0.79}$	97L,
c	12.322(1)			96L2
$d_{0(1)-O(2)}$	3.007(5)			
$d_{0(1)-3\,B(1)}$	1.463 (1)			
a	5.3761(7)	T_{prep} = 1350 K	$B_6O_{0.83}$	97L
c	12.326(3)			
$d_{0(1)-O(2)}$	3.025(5)			96L2
$d_{0(1)-3\,B(1)}$	1.476 (1)			
a	5.3774(7)	T_{prep} = 1250 K	$B_6O_{0.84}$	97L
c	12.322(3)			
$d_{O(1)-O(2)}$	3.004(3)			
$d_{O(1)-3\,B(1)}$	1.476 (1)			
a	5.3862(3)		B_6O	91L2
c	12.319(1)			
c/*a*	2.29			
V	309.5 Å^3			
d	1.56		inter-icosahedral	
	1.81		intra-icosahedral	
	1.65		origin to 6 B(1)	
	1.80		origin to 6 B(2)	
	3.06		X – X (chain)	
	1.50		X – 3 B(1)	
a	5.390(1)	*T* = 300 K	$B_6O_{0.96}$ (high-pressure synthesis)	97H
b	12.313(1)			
c/*a*	2.284			
V	309.8 Å^3			
a	5.3619(3)	*T* = 300 K	$B_6O_{0.72}$; nominal composition B_6O,	97O
c	12.3376(4)		sintered for 105 h at 1450 °C	
a/*c*	2.30			
a	5.3824(4)		$B_6O_{0.72}$; nominal comp. $B_{3.33}O$,	
c	12.322(1)		sintered for 105 h at 1450 °C	
a/*c*	2.29			
a	5.367(1)	*T* = 300 K	$B_6O_{0.76}$	93K
c	12.328(2)			
a/*c*	2.30			

Further lattice parameters of B_6O obtained from sintering amorphous B and B_2O_3, α-rhombohedral boron and B_2O_3 (at different *T*), respectively in [97L].

Dependence of the oxygen content on the preparation temperature in [97L].

occupancy of the position 6(c) O position

0.839(4)	*T* = 1250°C	97L
0.831(5)	*T* = 1350 °C	
0.787	*T* = 1450 °C	
0.76(6)		93K

Site determination of oxygen by O K_α investigation in [91K].

Oxygen occupancy of the 6(c) position vs. reaction temperature [97O].

O-O distance
(in Å)

d	2.5...3.5	*T* = 300 K	calculated fit to O K_α spectra	91K
	3.08	*T* = 300 K	X-ray diffraction	91H
	3.014		ab initio calculation	91L1

Electronic properties

p-type semiconductor

Calculated energy band structure in Fig. 1 [91L1].

Calculated electron density of states in Fig. 2 [94B2].

Electronic structure and optical properties of $B_{12}O_2$ crystals [96L1].

B K_α fluorescence spectrum in Fig. 3 [97K2].

B and N K edges of B_6N (compared with the B and O K edges of B_6O) in Fig. 4 [97G1].

Lattice properties

U-symmetry IR phonon modes

Experimental [94K, 97W2] ν/c [cm^{-1}]	Oscillator strength $\Delta\varepsilon$	Damping constant γ [cm^{-1}]	Calculated [94B1] ν/c [cm^{-1}]	Symmetry type
1117			952	E_u
1047.3	1.506	40.5	1109 (strong)	E_u
(897)			942	A_{1u}
883.4	0.137	11.6	919 (strong)	A_{2u}
850.6	0.009	11.6	949	A_{2u}
783.1	0.063	11.6	756 (strong)	A_{2u}
731.0	0.011	7.7	518	E_u
713.6	0.080	9.6	681 (strong)	E_u
			510	A_{1u}
592.1	0.012	9.6	508	E_u
511.6	0.008	6.8	69	A_{2u}
408.9	0.099	8.2	386 (strong)	E_u
(301)				
(270)				

Correlation between the experimentally determined phonon and the calculated ones: The attribution of the five strongest phonons seemed inevitable. The weak phonons were attributed according to their sequence in frequency. Uncertain phonons in parentheses.

resonance wavenumbers of the Raman active phonons

(Strong and weak excitation intensities differ by a factor 1.3 [94K, 97W1].)

Uncertain resonance wavenumbers and error margins in parentheses.

ν/c (weak excitation) [cm^{-1}]	ν/c (strong excitation) [cm^{-1}]	Raman scattering intensity
264(5)	264(5)	weak
398(6)	396	weak
521	519	weak
530	534	weak
556	555	weak
639(10)	627	weak
(773)		
902(10)	909	strong
1034(16)	1034(20)	strong
1119		medium
(1243)		weak

thermal expansion coefficient

α	$5.5 \cdot 10^{-6}\ K^{-1}$	79B

Optical properties

IR reflectivity and absorption spectra of B_6O in Fig. 5 [92K, 94K, 97W2].

IR reflectivity and absorption spectra also in [87W1] and [87W2].

FT Raman spectrum in Fig. 6 [97W2].

Further properties

Thermodynamic functions of B_6O in [91T1].

C_p, heat capacity; S, entropy; $(G - H_0)/T$, reduced thermodynamic potential, $H_T - H_0$ and $H_T - H_{298.15}$, enthalpy [91T1]

T [K]	C_p [cal mol^{-1} K^{-1}]	S [cal mol^{-1} K^{-1}]	$(G - H_0)/T$ [cal mol^{-1} K^{-1}]	$H_T - H_0$ [cal mol^{-1}]
15	0.0164	0.00595	0.00149	0.0672
20	0.0336	0.0129	0.00343	0 1893
25	0.0572	0.0228	0.00626	0.4135
30	0.0871	0.0358	0.01006	0.7716
35	0.1172	0.0512	0.01479	1.2730
40	0.1629	0.0697	0.02047	1.9673
45	0.2229	0.0923	0.02715	2.925
50	0.297	0.1194	0.03498	4.219
60	0.489	0.1895	0.05461	8.102
70	0.738	0.283	0.08019	14.19
80	1.043	0.401	0.1127	23.04
90	1.412	0.544	0.1524	35.24
100	1.852	0.715	0.1999	51.51
120	2.925	1.144	0.3197	98.85
140	4.238	1.689	0.4747	170.11
160	5.752	2.353	0.6680	269.60
180	7.419	3.125	0.8963	401.2
200	9.184	3.998	1.1616	567.0
220	10.99	4.958	1.464	768.5
240	12.80	5.992	1.797	1006.5
260	14.56	7.09	2.162	1280.5
273.15	15.68	7.83	2.416	1479
280	16.26	8.23	2.554	1589
298.15	17.76	9.30	2.931	1898
300	17.91	9.41	2.971	1931
310	18.72	10.01	3.189	2114
377.2	21.00			1660
409.3	22.24			2472
463.1	23.45			3870
520.5	25.86			5752
564.3	27.10			7214
616.1	27.76			8828
679 . 9	29.90			11416
721.2	31.17			13188
781 .8	32.31			15630

temperature dependence of C_p

C_p (B_6O) = 46.53 + 133.64·10^{-3} T + 0.04·10^5 T^2, T in K 86M

enthalpy

(in kJ mol^{-1})

H	–527(32)	T = 300 K	standard, calculated	86M
	–1730(32)	T = 393 K	dissolution in aqu. sol. of HNO_3	

Temperature dependence of the heat capacity in Fig. 7 [91T1].

Thermoelastic properties approximately determined by empiric functions [91T2].

thermoeleastic properties of boron suboxide (from [92T])

α, thermal expansion coefficient; V, mole volume; γ, Grüneisen parameter; δ_s, adiabatic Anderson-Grüneisen parameter; δ_t, isothermal Anderson-Grüneisen parameter; $(\partial B_S/\partial p)_T$, Murnaghan parameter; Θ_D, Debye temperature

T [K]	α [10^{-6} K^{-1}]	V [cm^3mol^{-1}]	γ	δ_s	δ_t	$(\partial B_S/\partial p)_T$	Θ_D [K] [1])
0	0	31.075	-	-	-	-	1490
50	0.134	31.0755	0.744	1.55	4.17	2.29	1490
100	0.837	31.076	0.771	1.50	4.27	2.27	1490
150	2.256	31.078	0.769	1.50	4.12	2.27	1490
200	4.139	31.083	0.766	1.51	3.99	2.27	1489
250	6.14	31.764	091 0	1.51	3.79	2.28	1489
298	7.95	31.102	0.760	1.58	3.64	2.34	1489
400	12.48	31.135	0.836	1.38	3.44	2.23	1488
500	14.94	31.178	0.818	1.41	3.24	2.24	1486
600	16.65	31.227	0.786	1.47	3.12	2~28	1485
700	18.00	31.281	0.752	1.54	3.05	2.32	1483
800	19.17	31.339	0.721	1.61	3.02	2.36	1480
900	20.22	31.400	0.692	1.68	3.01	2.40	1478
1000	21.21	31.464	0.667	1.75	3.01	2.45	1476
1200	23.04	31.602	0.624	1.88	3.05	2.55	1469
1500	25.62	31.829	0.573	2.06	3.12	2.69	1459

[1]) For partly deviating values see Fig. 8 [91T1].

B_S, adiabatic bulk modulus; B_T, isothermal bulk modulus; G, shear modulus; E, Young's modulus, σ_s, poisson coefficient; v_{av}, average sound velocity

T [K]	B_S [Mbar]	B_T [Mbar]	G [Mbar]	E [Mbar]	ν [Mbar]	v_{av} [km s^{-1}]
0	2.28494	2.28494	2.04722	4.72925	0 155	9.747
50	2.2849	2.2849	2.04721	4.72922	0.155	9.747
100	2.2848	2.2847	2.04713	4.7290	0.155	9.746
150	2.2846	2.2852	2.0468	4.7284	0.155	9.746
200	2.284	2.283	2.0463	4.7271	0.155	9.746
250	2.283	2.280	2.0453	4.725	0.155	9.745
298	2.282	2.278	2.044	4.722	0.155	9.743
400	2.278	2.269	2.040	4.713	0.155	9.739
500	2.274	2.260	2.035	4.702	0.155	9.734
600	2.269	2.251	2.030	4.691	0.155	9.730
700	2.263	2.242	2.023	4.676	0.156	9.721
800	2.256	2.231	2.016	4.660	0.156	9.714
900	2.249	2.221	2.008	4.642	0 . 156	9.704
1000	2.241	2.210	2.000	4.624	0.156	9.695
1200	2.223	2.185	1.980	4. 580	0.157	9.668
1500	2.191	2.144	1.947	4.506	0.157	9.622

Temperature dependence of the Debye temperature in Fig. 8 [91T1].

Influence of annealing on the mechanical moduli (elastic and shear) in [91T2].

bulk modulus
(in GPa)

B_0	222	T = 300 K	theoretical	92L
	228		exp.	92T
	38			97L

microhardness

H_K	3020 kg mm^{-2}	88W

internal friction

Temperature dependence of internal friction in Fig. 9 [91T2].

chemical reactivity

Reactivity of boron suboxide (B_6O) [87U].

Further references

Preparation [77G], crystalline structure: [61L, 66L, 65M, 76B], thermal conductivity, physicochemical properties [79B], X-ray emission [71P], thermal properties [73P], electrical conductivity [70W]

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Fig. 1.

$B_{12}O_2$. Calculated energy band structure. The solid (dashed) lines represent states even (odd) under reflection. The dotted-dashed line along the threefold ΓZ rotation axis are the doubly degenerate representation. The + and – at symmetry points represent the symmetry under inversion. [91L1].

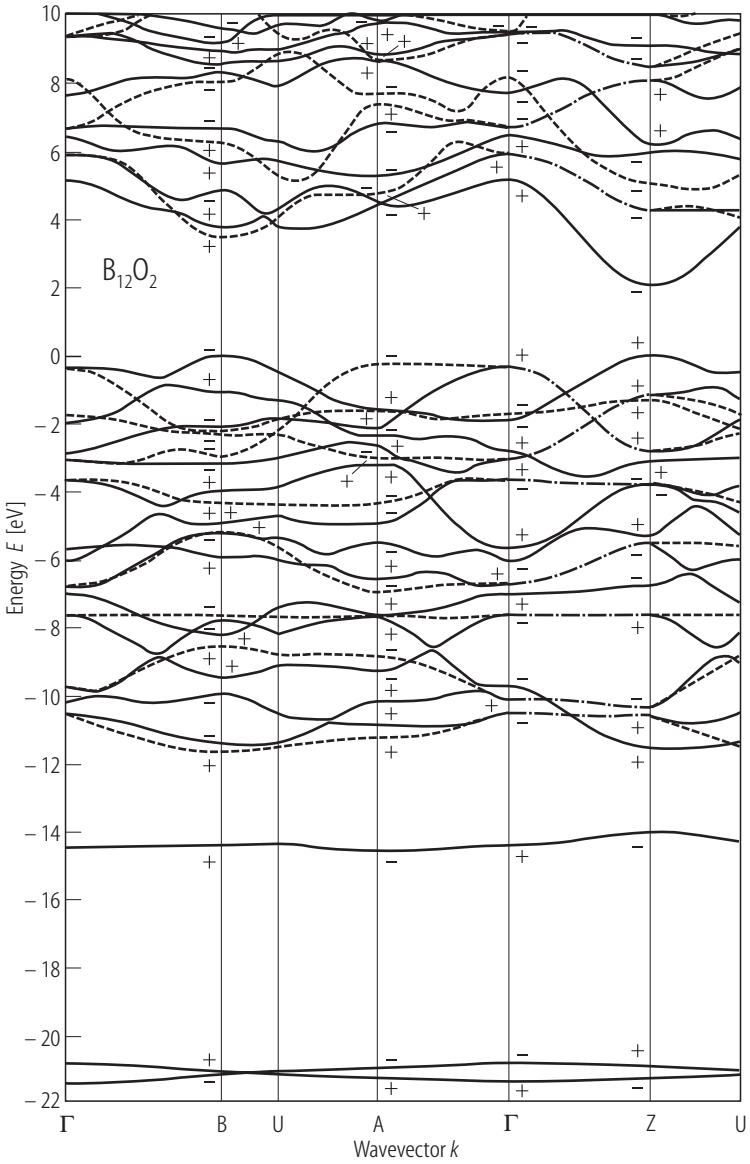

Fig. 2.

$B_{12}O_2$. Calculated density of states for electrons [94B2].

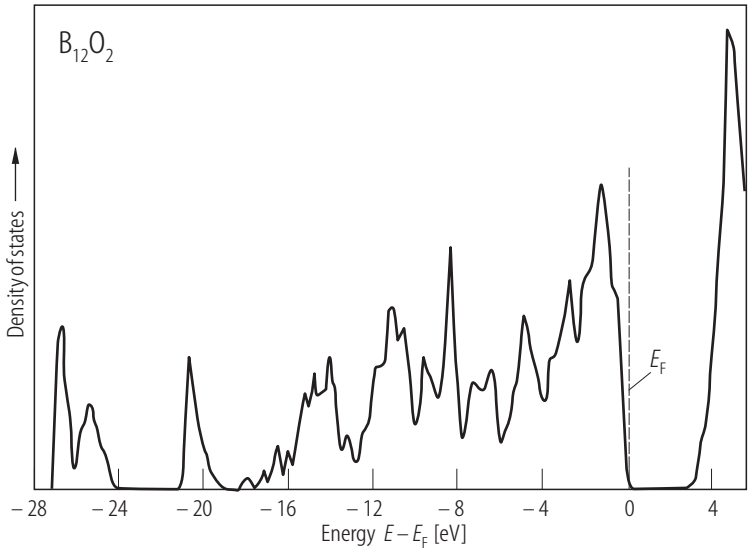

Fig. 3.

$B_{12}O_2$. B K_α X-ray fluorescence spectra [97K1]. The incident X-ray energy was changed by varying the magnetic gap of the undulator. A change of the gap from 91 to 105 mm corresponds to the photon energy of the undulator's first harmonic from 185 to 271 eV.

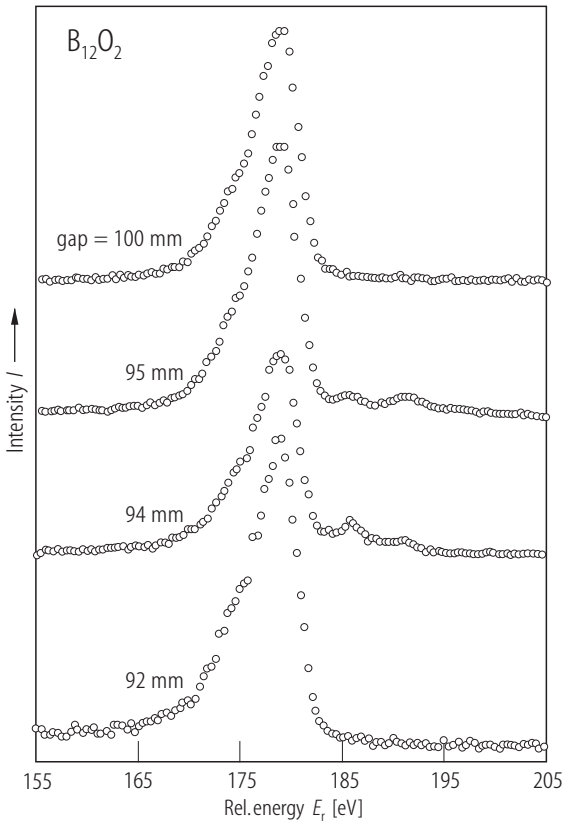

Fig. 4.

B_6N, B_6O. B and O K edges of B_6O compared with B and N K edges of B_6N aligned on a relative energy scale. The estimated onset of the conduction band is at 0 eV [97G1].

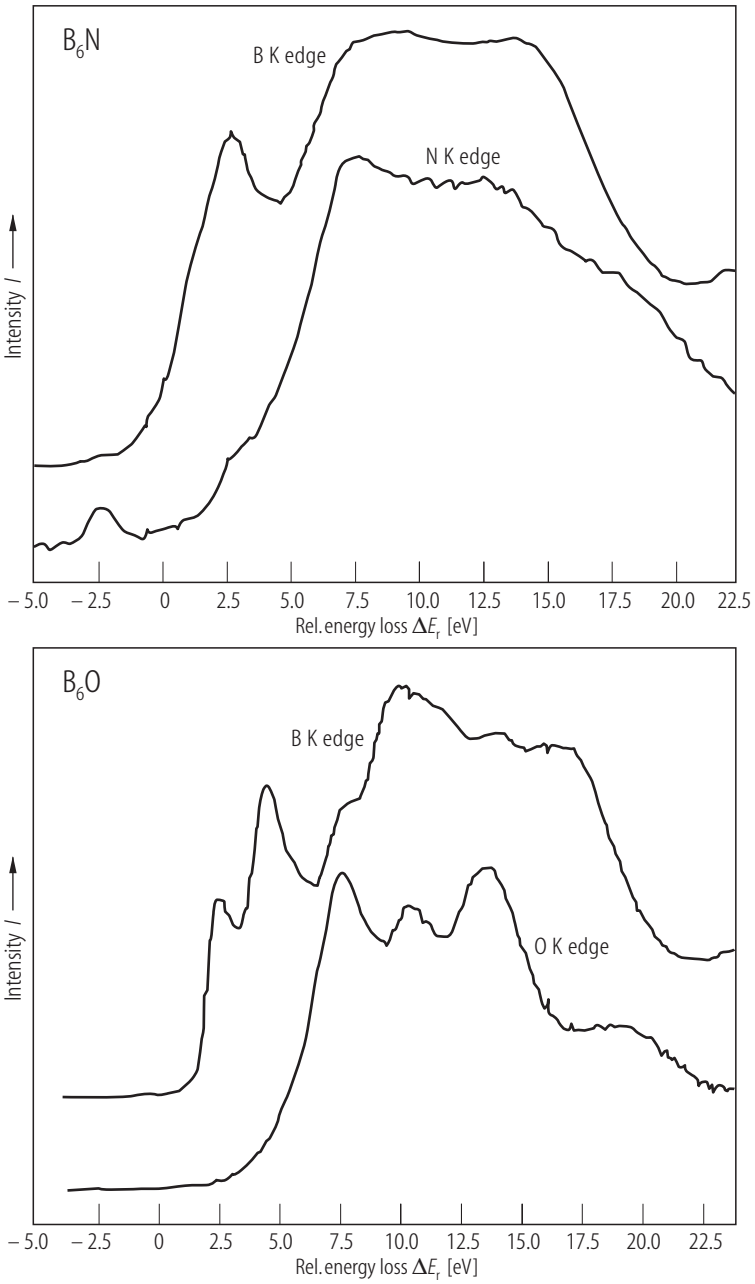

Fig. 5.

$B_{12}O_2$. Reflectivity and absorption index vs. wavenumber [92K, 94K, 97W2].

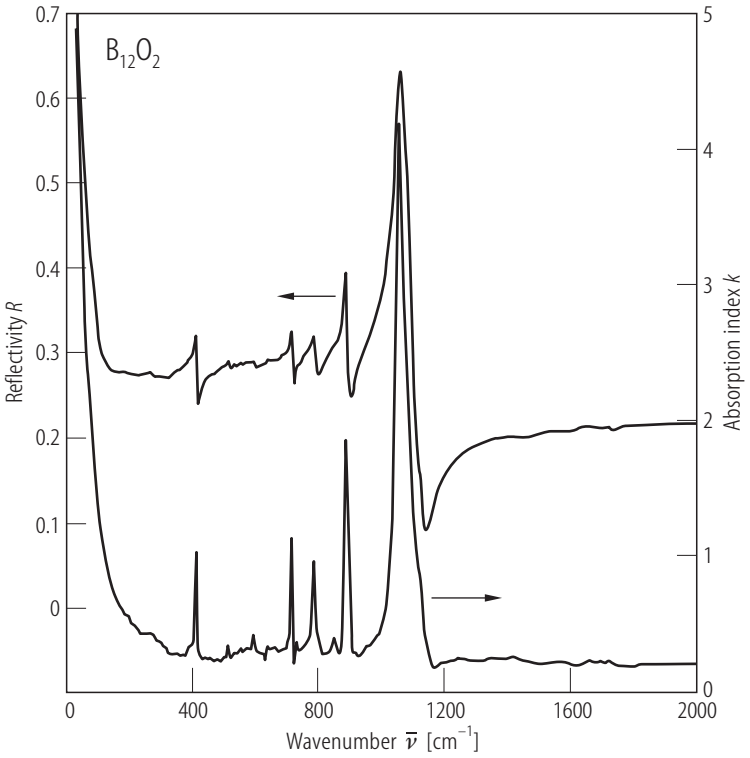

Fig. 6.

$B_{12}O_2$. FT-Raman spectrum vs. Raman shift with different excitation intensities of the Nd:YAG laser (1W and 1.3 W respectively) [94K, 97W2].

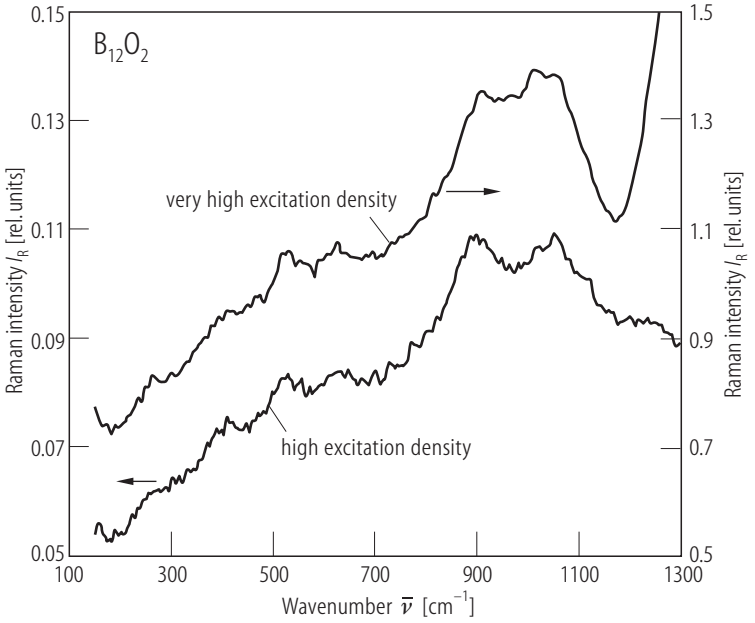

Fig. 7.

$B_{12}O_2$. Heat capacity vs. temperature; insert: low-temperature range [91T1].

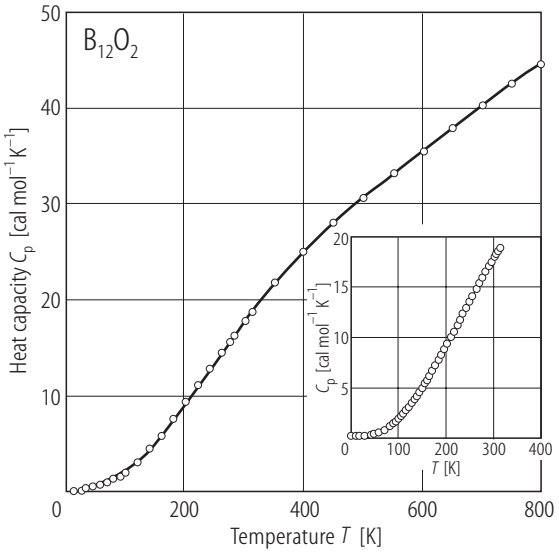

Fig. 8.

$B_{12}O_2$. Debye temperature vs. temperature [91T1].

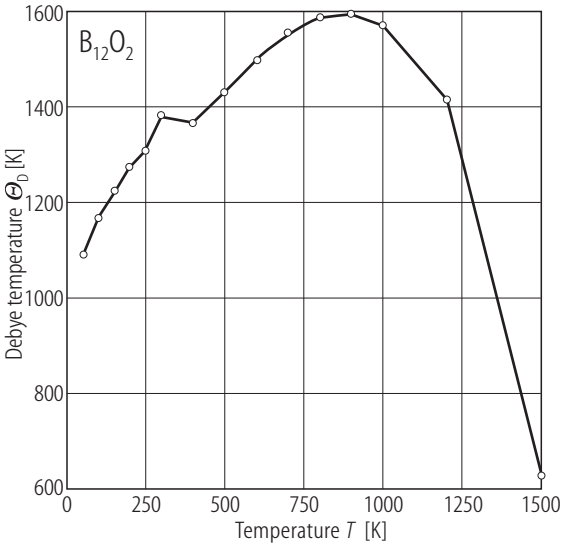

Fig. 9.

$B_{12}O_2$. Internal friction; Q^{-1} and f^2/f_0^2 vs. temperature. **(a)** Low temperature range; **(b)** high temperature range [91T2]. 1: initial sample, 2: sample after 2 h annealing in vacuum at 970 K.