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X-ray study of the synthesis of boron oxides at high pressure: Phase diagram and equation of state

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A systematic study of the of boron/oxygen systems at high pressure and high temperature has been made using the diamond anvil cell and the Paris-Edinburgh large volume press. The phase diagrams at 3 GPa and 6 GPa are determined from in-situ x-ray measurements. The synthesis of B_2O_3 and B_6O only have been observed. No evidence was seen in these experiments for the previously reported B_2O compound over the range of pressures and temperatures studied, $P < 43$ GPa and $T < 2500$ K. The equations of state of orthorhombic B_2O_3 and B_6O have also been measured in quasihydrostatic medium to pressures exceeding 40 GPa. Implications for high-pressure material synthesis are discussed.

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I. INTRODUCTION

The utility of high pressure in material science has been clearly demonstrated and widely acknowledged with the first synthesis of diamond in 1955.[1] Attempts to develop materials with a combination of properties approaching, or even improving upon, those of diamond have generated important high-pressure research efforts. In particular, following the concept of compounds isoelectronic with carbon, the synthesis of B_2O with a diamondlike structure has been reported[2,3] but its existence is still to be confirmed.[4] Applying pressure changes the volume, the electronic density, the concentration of defects, and the microscopic arrangement of molecules.[5] In particular, increasing pressure is an excellent way to augment the chemical reactivity of molecules with strong covalent bonds. Some recent surprising results in the solid state chemistry of molecules CO_2,[6] N_2,[8] N_2O (Ref. 7) have launched a growing interest in the high-pressure synthesis of new materials with low-*Z* molecular reactants. Those materials are expected to have interesting properties such as high hardness, like cubic BN,[9] superconductivity, which has been shown in MgB_2,[10] or, high energy density storing, for example, as predicted in BH_3.[11] Boron is an important element for this new material science because of its unusual chemical bonding.

The experimental strategy to discover new high-pressure materials and to recover them at ambient pressure for technological use is being developed.[12] New possibilities should be examined by taking advantage of the third generation x-ray synchrotron sources and of modern high-pressure instrumental capabilities; like, for instance, the investigation of the stability of new compounds over a large *P-T* domain; the in-situ determination of the synthesis routes in *P*, *T* space, the study of direct elementary reactions or, determination of the best method to overcome the thermal activation barrier with temperature.

In this paper, we present a systematic study of the reactivity of boron and oxygen under pressure by using the third synchrotron source of the ESRF. By using a large volume press (LVP) and a diamond anvil cell (DAC) technology, respectively, coupled with resistive and laser heating, a large *P-T* domain has been explored. A stability diagram can be drawn from in-situ x-ray measurements. B_2O is never observed. The equations of state (EOS) of the recovered samples, B_2O_3 and B_6O, are determined. Finally, some new aspects of high-pressure (HP) material synthesis are discussed.

II. EXPERIMENTS

The experiments were carried out using a laser heated membrane DAC and a resistively heated Paris-Edinburgh LVP. Descriptions of these devices have already been published in great detail.[13] It is sufficient to point out that here some advantages and drawbacks of each technique in the perspective of high-pressure material research. The synchrotron x-ray diffraction technique used will also be described below.

The DAC remains the essential tool for a rapid exploration of the pressure-temperature phase diagram and for the identification of new high pressure phases. In the present study, mostly x-ray diffraction and optical visualization were used to characterize the in-situ properties of the materials. Pressures were measured with the hydrostatic ruby scale.[14] Elementary reactants, boron and oxygen, could be loaded. Yet, the precise stoichiometry of the initial reactants is difficult to control. For temperatures up to 1000 K, resistive heating of the DAC can be used to provide a uniform temperature in the sample chamber but in the present study much higher temperatures were needed. The samples were heated by a Nd:YAG laser (20 W) focussed on the sample. Heating was limited to the laser spot (~ 20 μm). It was difficult to gradually increase temperature before the reaction started. Also, the temperatures of the reaction could not be measured by pyrometry because the highly exothermic and rapid nature of the boron oxygen reaction generates flashes of light.

The LVP offers the possibility to study mm^3 samples. The quantities of the reactants can be exactly controlled and homogeneously mixed at the start. Resistive heating allows temperatures up to 2500 K to be reached, as measured by a

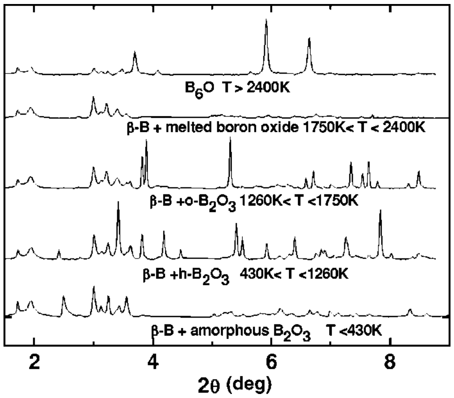

FIG. 1. Temperature evolution at 3 GPa of the x-ray diffraction pattern of a mixture of β-boron and amorphous B_2O_3, corresponding to a boron atomic fraction of 0.857. The x-ray patterns were measured in LVP with Sollers slits with a wavelength of 0.264 73 Å. The Rietveld refinement of these patterns could clearly identify the structural changes indicated in the figure.

thermocouple placed in the sample chamber. With the tungsten carbide anvils used, pressures were limited to below 10 GPa. A thin foil of Pt was stuck to the BN capsule that confines the sample, with the Pt and BN EOS being used to determine the pressure.[15] In the P-T range accessible, the synthesis environment of the LVP is better controlled than with the DAC. However, it is quite difficult to load gases in the LVP and hence to study the boron/oxygen elementary reactants.

X-ray diffraction patterns were collected in angle-dispersive geometry with a monochromatic beam and a MAR image plate detector. The DAC was equipped with boron seats, giving a large x-ray aperture of ±32°. A multichannel collimator, called Soller slits, optimized for the Paris-Edinburgh press was used to isolate the diffraction signal of the sample from the one of its complex environment (BN capsule, graphite heater, and boron epoxy gasket). It has allowed excellent improvements in terms of signal to background ratio.[16] The wavelength of the x-ray beam was selected equal to 0.3738 Å and to 0.172 98 Å or 0.264 73 Å, respectively, for the DAC and for the LVP measurements. The diffraction pattern of the sample was then measured in-situ with changing P-T conditions. In Fig. 1, the structural evolution of a mixture of β-boron and amorphous B_2O_3, corresponding to a boron atomic fraction of 0.857, is followed at 3 GPa by gradually changing temperature in steps of 100 °C. Structural changes are clearly observed. The Rietveld refinement of the x-ray patterns could unambiguously identify the sequence of phases. This is an in-situ observation of the chemical changes of B/O mixtures with P-T. Similar measurements with different stoichiometries, in between 0.4 and 1 boron atomic fraction, of the initial reactants are used to draw a tentative B/O phase diagram in the next section.

III. SYNTHESIS

A new synthesis route for boron oxides has been proposed some years ago by Yoo *et al.*[17] It is based on the direct reaction of boron and oxygen under pressure. Boron and oxygen are loaded in the DAC and a YAG laser-heating provides a way to overcome the activation barrier. A synthesis at 6.9 GPa was reported with a threshold for boron reacting with oxygen of approximately 2300 K. The product was identified as B_2O_3, in a mixture of its low-pressure (hexagonal) and high-pressure (orthorhombic) phases. We have attempted to modify the final products of the elementary reaction of boron and oxygen by changing the B/O_2 ratio in the sample chamber, as well as the initial pressure. Several DACs were loaded with boron powder or boron crystals in oxygen and the reaction was induced at various pressures ranging from 3.74 GPa to 43 GPa. Each sample was laser heated for several minutes by moving the Nd:YAG laser spot across the sample chamber until the reaction was completed. As summarized in Table I, in all cases the final product was orthorhombic B_2O_3 with, eventually, some residual boron and oxygen. A last loading was done with amorphous B_2O_3 as the oxidizing agent. In that case, after the reaction at 20 GPa, the sample pattern showed weak peaks of B_6O together with epsilon-oxygen and residual boron. It can be concluded that in a mixture of elementary reactants, there is a constant supply of oxygen at the laser spot and that an oxide with the maximum oxygen fraction is synthesized, namely B_2O_3. Whereas, when B_2O_3 is used as the oxidizing agent of boron, the possibility to reduce the O content of the oxide is forced and B_6O is obtained.

TABLE I. Summary of the various synthesis runs with the DAC.

P(GPa)	Reactants	Recovered products
3.75	Boron powder + oxygen	o-B_2O_3 + β-boron
5.6	Boron powder + oxygen	o-B_2O_3 + β-boron
5.9	Piece of boron + oxygen	o-B_2O_3 + oxygen
11	Boron powder + oxygen	o-B_2O_3 + β-boron
43	Boron powder + oxygen	o-B_2O_3 + β-boron
21	Boron powder + B_2O_3 powder	B_60 + β-boron + oxygen

The LVP allows that an accurate control of the stoichiometry of the reactant mixtures can be carefully weighed and intimately mixed before loading. Three different mixtures of β-boron and B_2O_3 were studied in stoichiometric mixtures corresponding to B_6O, $B_{2.81}O$, and B_2O chemistries. The reactivity of these mixtures was studied at two pressures, 3 GPa and 6 GPa. Temperature was increased in steps of 100 °C and the temperature was held constant for between 15 mn and 30 mn. The structural evolution of the sample was clearly identified from the diffraction pattern at various temperatures, as shown in Fig. 1. These data are used in conjunction with thermodynamic considerations to draft a phase diagram of the B/O system, over the boron atomic fraction concentration ranges between 0.4 and 1, at 3 GPa and at 6 GPa, as presented in Fig. 2. The sequence with temperature of oxides in equilibrium with β-boron is the following: amorphous B_2O_3, hexagonal B_2O_3, orthorhombic B_2O_3, fluid oxide and B_6O. B_2O is never observed. That essentially confirms previous studies. Srikanth *et al.*[18] showed that B, B_2O_3, and B_6O were the only phases present

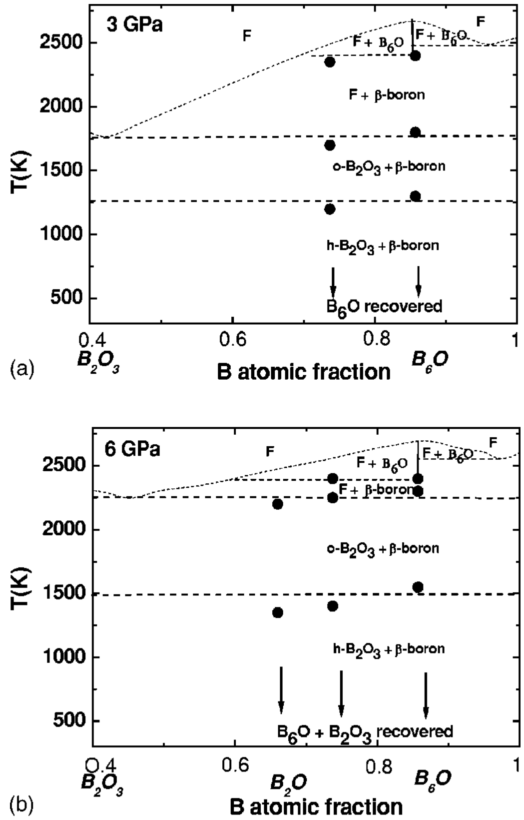

FIG. 2. Phase diagram of the B/O mixtures at 3 GPa and 6 GPa. The diagrams are drawn from measurements done at three boron concentrations, 0.857, 0.737, and 0.66. The dots indicates the temperature at which structural changes were clearly identified. The dashed lines indicate boundary lines compatible with observation. The arrows point to the recovered samples at ambient temperature and pressure.

when B/B_2O_3 ratios were reacted at temperatures from 1200 °C to 1700 °C and pressures up to 1.5 GPa. Hubert *et al.*[19] observed that when the mixtures of B/B_2O_3 are submitted from 1500 °C to 1800 °C and pressures above 6 GPa B_6O and the three different B_2O_3 polymorphs were recovered. However, attempts to synthesize the diamond form of B_2O, even by following Endo's preparation method,[3] were unsuccessful. The *P*-*T* domain of investigation is slightly extended here. More importantly, we can follow the in-situ growth of the compounds by x-ray diffraction. The result is that in Fig. 2 we can see that B_6O is grown from the melt. Also, with pressure, the fluid domain in between the stability domains of B_2O_3 and B_6O decreases and should disappear above 8 GPa. Consequently, the synthesis of B_6O in the DAC at 20 GPa was certainly obtained directly via the solid phase. A surprising result is that, for equal initial stoichiometries, the reaction ratio is higher at 3 GPa than at 6 GPa as can be seen from the phases present upon quenching. Our study confirms the idea that the reduction of B_2O_3 by boron leading to the crystallization of B_6O is favored when boron oxide is molten and boron atoms are in solution. Furthermore, in all three experiments performed at 6 GPa, B_2O_3 (orthorhombic structure) is always recovered with B_6O. Instead, B_6O only is recovered at 3 GPa with no B_2O_3.

TABLE II. Data of the equation of state of orthorhombic B_2O_3 at 298 K. The volume of the unit cell (containing 4 B_2O_3 molecular units) is in Å^3, with an error of typically ±0.6 Å^3. *P*, the pressure is in GPa, with an uncertainty ±1 GPa.

P (GPa)	*V* (Å^3)
0	149.3
12.16	139.8
19.6	136.1
22.5	133.5
24.7	131.2
28.0	129.7
29.7	128.6
32	127.5
34	126.3
35.7	125.9
37.8	125.1
40.0	124.1
41.5	123.7

IV. MEASUREMENT OF THE EQUATION OF STATE

A. Equation of state of B_2O_3

Boric oxide, B_2O_3, was only known in the glassy form for a long time. The forms of B_2O_3 now known include, glassy, liquid, hexagonal, and orthorhombic. Liquid and glassy B_2O_3 are complex structures that consist of randomly distributed trigonal BO_3 units and boroxol B_3O_6 rings and some work is still being done to clarify different aspects of it.[20] In contrast to the vast interest in borate glasses, there exist few investigations on crystalline B_2O_3. Spontaneous crystallization of B_2O_3 is not a simple process. The low-pressure structure of B_2O_3, with a hexagonal unit cell, was obtained by Gurr *et al.*[21] It results from the arrangement of an infinite chain of

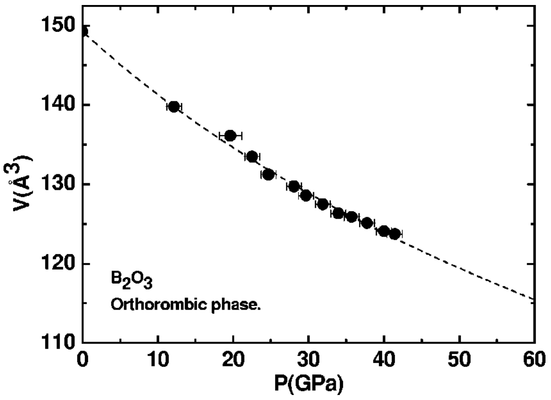

FIG. 3. Volume of the unit cell of orthorhombic B_2O_3 versus hydrostatic pressure obtained on decompression, after in-situ synthesis. Uncertainty in the fit is essentially due to the error bar of the pressure measurement. The dashed line is the Vinet fit of the data, $P(\mathrm{GPa})=3B_0(1-X)X^{-2}\exp(3(B_0'-1)(1-X)/2)$, with $X=V/V_0$ and $V_0=149.3$ Å^3, $B_0=169.9$ GPa and $B_0'=2.54$. No data points were measured below 10 GPa because of a sudden loss of pressure on the sample upon decreasing the pressure.

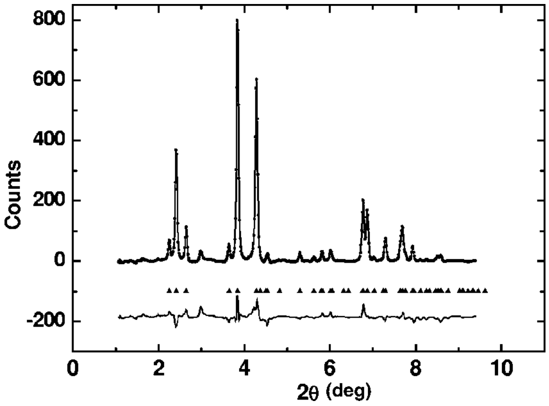

FIG. 4. The Rietveld refined diffraction pattern (measured at 0.1730 Å) of the recovered B_6O crystal, used for the EOS measurement in the Ne pressure transmitting medium.

BO_3 interconnected triangles. The high-pressure phase of B_2O_3 was obtained at a pressure of 6.5 GPa and a temperature of 1100 °C by Prewitt and Shannon.[22] It has an orthorhombic unit cell built up by two sets of tetrahedra with shared corners. So, under pressure, crystal B_2O_3 undergoes a structural transformation that increases the boron coordination from BO_3 triangular unit into the BO_4 tetrahedral unit.

TABLE III. List of the reflections of the x-ray spectra at ambient pressure of B_6O recovered from the high-*P*–high-*T* synthesis. The *hkl* indices correspond to the hexagonal setting of the rhombohedral structure. The parameters of the Rietveld refinement of the x-ray diffraction pattern are $a=5.425(9)$ Å and $c=12.328(24)$ Å and a volume of $314.3(9)$Å^3 for the hexagonal unit cell.

(*hkl*)	*d* spacings (Å)
101	4.4001
003	4.1123
012	3.7404
110	2.7186
104	2.5796
021	2.3144
015	2.1804
024	1.8706
211	1.7640
205	1.7039
107	1.6471
018	1.4647
303	1.4426
027	1.4104
220	1.3586
131	1.2903
223	1.2750
312	1.2517
217	1.2227
134	1.2017
128	1.1653
042	1.1546

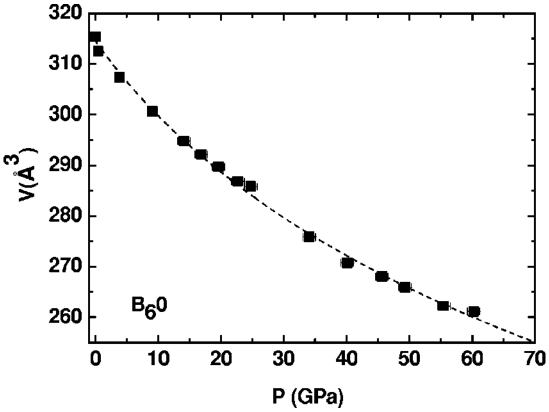

FIG. 5. Volume of the unit cell of B_6O in the hexagonal setting of the rhombohedral structure. The dots are x-ray data. Uncertainty is essentially due to the error bar of the pressure measurement. The dashed line is the Vinet fit of the data, $P(\text{GPa})=3B_0(1-X)X^{-2}\exp(3(B_0'-1)(1-X)/2)$, with $X=V/V_0$ and $V_0=314.5$ Å^3, $B_0=181$ GPa and $B_0'=6.0$.

The high-pressure orthorhombic phase of B_2O_3 can be metastably recovered at ambient pressure.

The EOS of orthorhombic B_2O_3 was measured under decompression in the oxygen pressure transmitting medium. The synthesis was obtained by laser heating a small piece of boron in oxygen at 41 GPa. The reaction was observed by x-ray diffraction to be complete. The Rietveld refinement of the diffraction pattern indicates a mixture of orthorhombic B_2O_3 and epsilon oxygen. The unit-cell volume of orthorhombic B_2O_3, as presented in Table II, was estimated versus pressure by following eight reflections (doing a least-squares fit of *d* spacing). The $V(P)$ data are plotted in Fig. 3. A Vinet formulation[23] of the EOS is used to reproduce the data with the following parameters: $V_0=149.3(9)$ Å^3, $B_0=169.9$ GPa, $B_0'=2.5$ corresponding, respectively, to the zero pressure volume of the unit cell (with 4 B_2O_3 units), the bulk modulus and its pressure derivative at ambient pressure. The zero pressure volume is in good agreement with previous determinations of Prewitt[22] ($V_0=148.6$ Å^3) and of Yoo[24] ($V_0=147.6$ Å^3). This is the first experimental determination for B_0 and B_0'.

B. Equation of state of B_6O

Boron suboxide, B_6O, has been extensively studied, especially because of the interest it raises as a superhard material. The study of boron suboxide has been difficult because room-pressure syntheses produced O-deficient compounds. Hence, there has been much uncertainty in the stoichiometry of B_6O. The system was investigated by Rizzo *et al.*[25] who assigned a B_6O formula using the rhombohedral unit cell. It was recently shown that high-pressure–high-temperature growth is critical to improve the stoichiometry and the crystallinity of boron suboxide,[19] now presented as nominally being B_6O. B_6O is described as a boron rich solid with a structure based on that of α-rhombohedral boron. This structure consists of eight B_{12} icosahedra situated at the vertices of a rhombohedral unit cell with two O atoms located in the

TABLE IV. Data of the equation of state of B_6O measured at 298 K in Ne pressure medium. The volume of the unit cell (in the hexagonal setting with 6 B_6O molecular units) is in Å^3, with a typical error of ±1.2 Å^3. P, the pressure is in GPa, with the uncertainty no greater than ±1 GPa above 10 GPa and ±0.3 GPa below.

P (GPa)	V (Å^3)
0	314.3
0.43	312.6
3.8	307.4
9.0	300.6
14.1	294.8
16.9	292.1
19.6	289.7
22.7	286.8
24.7	285.8
34.1	275.8
40.1	270.7
45.6	268.0
49.3	265.9
55.5	262.2
60.2	261.1

interstices along [111] rhombohedral direction. The EOS of B_6O is measured here with a small crystal taken from the recovered compound grown in the LVP at 3 GPa and 2400 K. X-ray fluorescence analysis of the recovered sample and the Rietveld refinement of its x-ray diffraction patterns, as shown in Fig. 4, confirms the B_6O stoichiometry with the rhombohedral cell. The list of observed reflections is presented in Table III. The parameters of the unit cell in the hexagonal setting (with 6 B_6O molecular units), obtained using these reflections, are $a_0 = 5.425(9)$ Å, $c_0 = 12.328(24)$ Å, and $V_0 = 314.3(9)$ Å^3. This value of V_0 is slightly larger than the ones reported previously.[19,26] It has been shown that the formula for the B_6O compound grown at high P-T is best reported as B_6O_{1-x} and that the cell volume is expected to increase with increase in O occupancy.[19] Insertion of O atoms in the interstitial sites, i.e., increasing the O occupancy, results in a cell volume expansion. A small size (15 μm) crystal of B_6O was pressurized in the DAC, embedded in Ne to provide a reasonable hydrostatic medium up to 50 GPa. The data of the volume of B_6O versus pressure are presented in Table IV and are plotted in Fig. 5. A Vinet formulation of the EOS reproduces very well the data with the following parameters, $V_0 = 314.5(8)$ Å^3, $B_0 = 181(5)$ GPa, and $B_0' = 6.0$.

The parameters of the equation of state of α-boron,[27] B_4C,[28] and B_6O, all related to the same rhombohedral structure are compared in Table V. The difference in V_0 is easily understood. Insertion of atoms in the interstitial sites of the α-boron structure results in a cell volume expansion proportional to the size of the atom occupying these sites. However, the bulk modulus of the three compounds have quite similar values, the one of B_6O being slightly smaller that could seem at odds with a greater hardness. But, as well known, the bulk modulus alone cannot explain the difference in hardness between compounds.[9] In fact here, the difference in hardness between these compounds must be sought in the intericosahedral atoms. In B_6O and B_4C, O atoms and C atoms are placed between icosahedra, linking them with strong covalent bonds. These intracluster bonds are stronger in B_6O than in B_4C, due to the higher electronegativity of oxygen relative to carbon, explaining why B_6O is a harder material. On the other hand, it seems that interstitial atoms have a weak effect on compressibility. The compressibility of the compound is thus the one of the α-boron structure.

TABLE V. Comparison of the unit cell volume, V_0, the bulk modulus, B_0, and the pressure derivative of the bulk modulus, B_0' of three compounds related to the same rhombohedral structure of α-boron.

Compound	V_0 (Å^3)	B_0 (GPa)	B_0'	Reference
α-boron	264.1	213 (15)	4	27
B_4C	328.5	199 (7)	1	28
B_6O	314.5	181 (5)	6	Present work

V. CONCLUSION

The B/O systems have been studied in a wide range of temperature and pressure. Properties of boron oxides determined in the present study are the following: The B/O phase diagram is constructed by using the well-characterized thermodynamic conditions of the LVP and in-situ x-ray diffraction; the stability P-T domains of the various boron oxides are determined; B_2O has not been synthesized in the P-T domain covered by our experiments (43 GPa, 2500 K); the equations of state of B_2O_3 and B_6O is measured under quasihydrostatic conditions, using O_2 and Ne media.

In the perspective of material synthesis under pressure, the comparison between the synthesis routes of the B/O mixtures in the DAC and in the LVP seems interesting. It is shown that with the DAC, the mesoscopic state of the reactants have a direct influence on the products obtained. With a mixture of O_2 and boron, B_2O_3 is always obtained because O_2 is in excess at the reaction site within the laser spot. Whereas, with a mixture of B_2O_3 and B, B_6O is obtained. On the other hand, using a LVP, synthesis conditions are better controlled. Elementary reactions are, however, not possible. Consequently, both devices are needed for a complete investigation of materials synthesis at high pressure.

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