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Structure and Bulk Modulus of High-Strength Boron Compounds

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The structures and homogeneity ranges of B_6O_{1-x} and $B_{12}S_{2-x}$ were studied using Rietveld analysis of powder X ray patterns. The oxygen content of boron suboxide decreases with temperature in the range 1250–1450°C. Stoichiometric boron suboxide cannot be prepared from amorphous or α-rh boron and B_2O_3 at ambient pressure. Significantly higher pressures are required. The boron subsulfide was found to be stable from $B_{12}S_{<1}$ to $B_{12}S_{1.3}$ at 1400–1600 °C. Semiempirical bulk modulus calculations are reported for hard icosahedral boron-rich compounds and diamond-like tetrahedrally coordinated boron compounds. In connection with this the structure of diamond-like B_2O is discussed.

1. INTRODUCTION

Superhard materials, formed between light elements, display a great variety of properties which are of fundamental as well as technological interest. Among these properties are great hardness, low mass density, high mechanical strength, high thermal conductivity, high chemical inertness, and excellent wear resistance. In addition, the materials include semiconductors, useable also at high temperatures, and strongly neutron-absorbing materials. The materials so characterized often contain boron as one component, for instance c-BN, B_4C, and B_6O.

Structurally these materials either belong to the tetrahedrally coordinated, diamond-related group of compounds or they belong to the icosahedral, boron-rich group of compounds. The former group includes representatives of the sphalerite and wurtzite types of structure, for instance BN, BP, $BeSiN_2$ (superstructure), and SiC (1). The second group includes representatives of many structure types, although the most prominent ones are structures related to that of boron carbide and the boron modifications (2–4). In the present contribution some new structural data on the boron suboxide B_6O and boron subsulfide $B_{12}S$ are included as well as a discussion of hardness and bulk moduli of some superhard materials.

2. STRUCTURES

2.1. *General Characteristics*

The structures of the majority of refractory boron-rich compounds are characterized by a three-dimensional, rigid boron network, consisting of slightly distorted boron icosahedra. The B_4C-type structure and variants is frequently described in the hexagonal system (space group $R\bar{3}m$, space group 166) with the trigonal axis of the icosahedron parallel to the *c* axis of the hexagonal unit cell. The three boron atoms closest to the trigonal axis, the rhombohedral boron atoms, bind directly to such atoms in neighboring icosahedra while the equitorial boron atoms bind to each other via nonboron atoms in, the instance B_4C, B_6O, and $B_{12}S_{2-x}$, and via three-center boron bonds in α-rhombohedral boron. The icosahedral boron network is relatively similar in the different representatives of the structure family of B_4C. The elongated hole along the *c* direction is, however, empty in α-rh boron, filled with three-atom C–B–C or C–B–B chains (occasionally empty in some unit cells) in B_4C (5), and occupied by two nonboron atoms in $B_{2.89}Si$, B_6P, B_6As, and B_6O_{1-x}.

In the diamond-like structures the average number of valency electrons per atom is four and each atom coordinates four neighbours at the corners of a tetrahedron. This tetrahedron is occasionally distorted, in particular when the compound is formed between components situated unsymmetrically around the group 14 (carbon group) elements in the Periodic Table. Materials of this type are anticipated to be very hard.

2.2. *Experimental*

Samples of B_6O_{1-x} and B_6S_{1-x} were investigated by Rietveld full-profile refinements of powder X ray data recorded in a Siemens D-5000 and a Stoe PSD diffractometer, respectively. The boron subsulfide was prepared by melting the elements in a high-frequency furnace under an argon atmosphere (sample B) as described in Ref. (6) or in a closed tantalum crucible (welded-on lid) (sample A) (7). The boron suboxide was prepared by reaction sintering *ex-iodide* amorphous boron or α-boron and B_2O_3 powders under an

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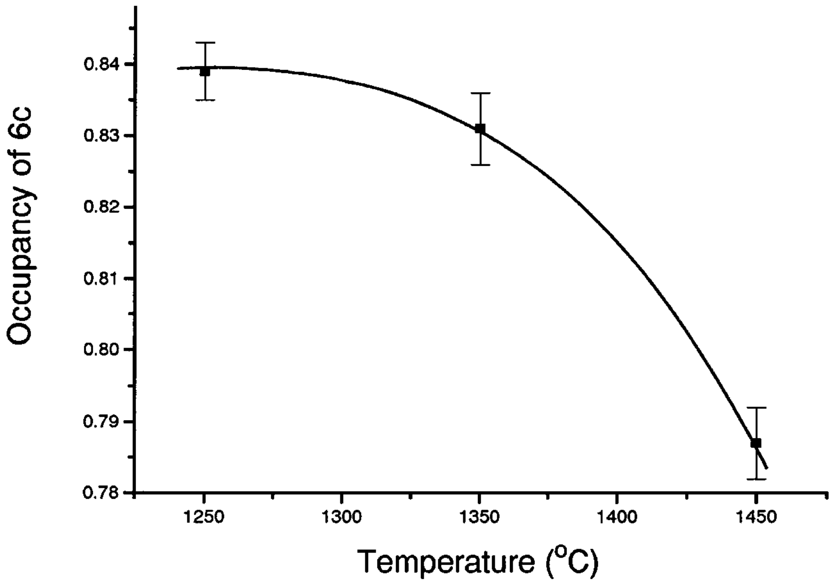

FIG. 1. Oxygen content (occupancy of position 6*c*) of B_6O vs temperature.

argon atmosphere at ambient pressure in a BN crucible at temperatures 1250–1450°C. In this manner different oxygen concentrations were obtained in the suboxide (8).

2.3. B_6O

The first structure determinations of B_6O did not indicate partial occupancy of the oxygen position (9, 10). Later it was shown (11), however, that oxidation of boron with ZnO at a temperature above 1350°C led to a partial occupancy of the oxygen position of 0.76. In the present study it was found that the oxygen concentration is solid B_6O decreases with temperature in the range 1250–1450°C as anticipated (Fig. 1). The cell dimensions, occupancy of the 6*c* position by oxygen and some interatomic distances are shown in Table 1 for materials prepared at different temperatures and presumably not too far from equilibrium. At lower temperatures than 1250°C it is progressively more difficult to reach equilibrium, since the reaction rate decreases. It is therefore likely that stoichiometric B_6O cannot be prepared using oxygen of ambient pressure. The cell dimensions for the B_6O material that was prepared at high pressure/high temperature conditions were (12), however, $a = 5.435$ Å and $c = 12.415$ Å, which is substantially larger than the values shown in Table 1. This observation indicates that the oxygen content is significantly larger than in the samples prepared in the present study. A structural study of the material prepared at high pressure/high temperature is being carried out.

2.4. $B_{12}S$

In Table 1 crystallographic data for three different samples of $B_{12}S_{2-x}$ are also presented (7). Sample A, which was

TABLE 1
Crystallographic Data for Boron Suboxide and Boron Subsulfide Samples

Sample, comp.	*a* axis (Å)	*c* axis (Å)	Temp. (°C)	Occup. of pos. 6*c*	Dist. (Å) O(1)–O(1)	Dist. (Å) O(1)–3B(1)
B_6O_{1-x}						
I, $B_6O_{0.79}$	5.3824(4)	12.322(1)	1450	0.787(5)	3.007(5)	1.463(1)
II, $B_6O_{0.83}$	5.3761(7)	12.326(3)	1350	0.831(5)	3.025(5)	1.476(1)
III, $B_6O_{0.84}$	5.3774(7)	12.322(3)	1250	0.839(4)	3.004(5)	1.476(1)
					S(1)–S(1)	S(1)–3B(1)
$B_{12}S_{2-x}$						
A, $B_{12}S_{1.3}$	5.8624(9)	12.147(4)				
A′, $B_{12}S_{<1}$	5.583(2)	12.278(5)	1450			
D, $B_{12}S$	5.810(2)	11.94(2)		0.485(6)	2.191(5)	1.821(3)

prepared in a closed tantalum crucible, has a considerably larger unit cell volume than sample A′, which was prepared in the same manner as A but subsequently heat treated at 1450°C for 16 h in a high-frequency furnace. Substantial sulfur losses were noted during this heat treatment. Sample A thus represents a sulfur-rich (cell volume 361.5 Å^3) and sample A′ a sulfur-poor (cell volume 331.4 Å^3) composition of the phase $B_{12}S_{2-x}$. From chemical analysis is was evident that the approximate composition of the sulfur-rich phase is $B_{12}S_{1.3}$. Sample D, which was prepared according to the method described by Matkovich (6), had a unit cell volume in between the two extremes. Sample D was used to record the X ray intensities for the Rietveld structure refinement.

Since the occupancy of atomic position 6*c* is only 48.5(6)%, the composition of sample B corresponds to the formula $B_{12}S$, while the homogeneity range extends to lower as well as to higher sulfur contents, at least to $B_{12}S_{1.3}$. The composition obtained from the structure refinement of sample D agrees well with that reported by Matkovich (6). It is also seen from Table 1 that the S–S distance is 2.19 Å, which exceeds the Pauling “single bond” radius sum by only 0.1 Å, compatible with the occurrence of two sulfur atoms in the same unit cell.

2.5. B_2O

The occurrence of a refractory phase of composition B_2O was suggested a long time ago (1) in connection with a study of the graphite-like phase B_2O. The material was later (13) prepared at 1000–1200°C and 3.5–5.5 GPa from CrO_3 and BP. The compound was reported to crystallize in the space group P3 with the hexagonal unit cell $a = 2.879$ Å and $c = 7.052$ Å, containing four boron and two oxygen atoms. The structure was suggested to consist of buckled atomic layers (consisting either of boron atoms or of boron and oxygen atoms), stacked in the *c* direction (corresponding to [111] direction of the sphalerite cell) in the sequence BB layer and double OB–BO layer. In the present study a calculation of the interatomic distances was performed, using the space group P$\bar{3}$m1 with boron at the atomic positions 2*c* ($z = 0.375$) and 2*d* ($z = 0.042$), respectively, and oxygen at 2*d* ($z = 0.292$). These ideal coordinates, involving the assumption $d_{BB} = d_{BO}$, were used in the calculations, since our attempts to refine the structure parameters using the published data were not successful. The calculation shows that the B–B distances within and between the buckled boron layer are normal, namely 1.765 Å. The BO distances are, however, large within the two halves of the BO double layer, namely 1.765 Å, a consequence of the assumption made. If the half layers of the double layer are assumed to be plane the B–O distance is 1.66 Å, which is more reasonable considering the interatomic distances in other B–O solids. In B_6O it is, for instance, slightly less than 1.50 Å. The shortest B–O distance between a boron atom in the buckled boron layer and an oxygen atom in the buckled double layer is, however, as large as 2.35 Å, which indicates a very weak bonding between these two types of layers. This distance will be even larger if the BO half layers are assumed to be plane. The distances presented above indicate that the structure suggested (13) for B_2O has mainly properties characteristic of layer structures, including no great hardness. This conclusion agrees well with a quantum chemical, total energy study of the B_2O structure recently reported (14). In this study the conclusion was reached that the proposed structure for B_2O is unstable.

The densities of diamond and boron nitride are 3.51 and 3.49 g cm^{-3}, respectively. The measured mass density of B_2O was reported to be 2.48 g cm^{-3} in perfect agreement with the density calculated from the structure data (13). The density of B_2O is, however, anticipated to lie much closer to the densities of the isoelectronic compounds mentioned.

The crystal chemical analysis of the structure of B_2O presented above indicates that a reinvestigation of the structure is well motivated, in particular since only powder intensities were used and complete structural and refinement data were not published.

It is interesting to speculate about the structure along the following lines. Assume, that the unit cell volume of B_2O (50.62 Å^3) is correct and that the structure can be described in a cubic BN-like unit cell of the same volume. The cubic *a* axis is then 3.6992 Å. If this unit cell accommodates eight atoms (possibly not in the exact B/O ratio of 2) as in other sphalerite-type structures, the average interatomic nearest-neighbours distance in the structure is 1.60 Å and the density 3.29 g cm^{-3}, both values being more plausible than the values presented by Endo *et al.* (13).

3. BULK MODULUS AND MICROHARDNESS

3.1. Theoretical

The indentation (micro)hardness of a material can be used as a simple strength probe, although hardness is controlled by elastic as well as plastic deformation modes and hence influenced by elastic properties, dislocation density and mobility, and several other structural features (15, 16). Although there is no direct fundamental connection between hardness and bulk modulus of a material a relatively good correlation was evidenced between hardnesses and moduli for hard and superhard materials (16). The bulk modulus is, however, preferred since it is the simpler concept and in addition is accessible for *ab initio* as well as semiempirical calculations. Bulk moduli of diamond-like boron-containing structures were studied by *ab initio* calculations and the results were compared to experimental values (17, 18). It was found that the bulk modulus (B_0 GPa) depends strongly on the average interatomic distance (*d* Å)

TABLE 2
Bulk Moduli and Microhardnesses of Some Boron Compounds (in GPa)

Phase	Theoretical B_0	Ref.	Semiempirical B_0	Ref.	Exp. B_0	Ref.	Microhardness	Ref.
Diamond	435, 438	19	430		443	19	≈ 88	20
BN	367	21	367	21	465	19	60–75	22
BP	165	21	166	21	173, 267	21	34–36	20
BAs	145	23	128				19	20
B_2O			(319)				34–41	13
α-rh B	249, 207	24, 26	(399)		224	25		
β-rh B			(395)		185	25	34	20
B_4C	234	27	(366)		245	26	38	26
B_6P			(345)				30	28
B_6As	182	27	(336)					
B_6O	222	27	(385)		228	29	38	30

according to Cohen's formula (19),

$$B_0 = (N_c/4)(1971 - 220\lambda)d^{-3.5}, \qquad [1]$$

where λ includes correction for ionicity of bonding (λ equal to 1 for III–V and 2 for II–VI compounds) and N_c is the average number of nearest neighbors in the structure. For diamond-like structures N_c is equal to four, but it was found that the formula is also applicable to other structure types, e.g., Si_3N_4, if the correction factor $N_c/4$ is included.

3.2. Boron Compounds

Semiempirical calculations of bulk moduli were performed using the above formula. The average interatomic distances used were those obtained from crystal structure determinations, considering their respective frequency of occurrence in the structure. The results for boron compounds are presented in Table 2 together with some published data from *ab initio* calculations, experimental values, and microhardnesses.

The semiempirical value for the bulk modulus of B_2O was calculated with $d = 1.60$ Å, in agreement with the above discussion, and $\lambda = 1.5$, which is the average between a III–V and a II–VI compound. The distance is also close to the average of the radius sum of the van Vechten–Phillips tetrahedral covalent radii (31) for B–O (1.531 Å) and B–B (1.706 Å) interatomic bonds. Due to the assumptions made as regards the interatomic distance *d*, the uncertainty of the bulk modulus of B_2O is larger than that for the other tetrahedral compounds of Table 2. It seems, however, adequate to say that it lies between the moduli of BN and BP and that B_2O is a very interesting potential superhard material.

Recent publications on B_2O are somewhat inconsistent. The occurrence of B_2O was not corroborated in a recent study of B_xO compositions by Srikanth *et al.* (32), although the study covered the range $2/3 < x < 24$. Furthermore, the powder pattern of B_2O reported by Liu *et al.* (33) deviates strongly from that published by Endo *et al.* (13).

The semiempirical bulk moduli of boron-rich compounds are all significantly larger than the experimental values (see Table 2). This overestimation seems to depend in part on the large correction factor ($\sim 3/2$) for the number of nearest neighbors, which is approximately six, as compared to the four nearest neighbors in tetrahedrally coordinated structures. In addition, of course, the delocalized-electron bonding within the icosahedron differs greatly from the mainly covalent and partially ionic bonding in tetrahedral solids. Also the moduli of boron-rich compounds are essentially settled by the average B–B distance and therefore are not greatly different for elementary boron and for representatives of the boron carbide structure family.

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