Thermal stability of hexagonal OsB₂

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Abstract: The synthesis of novel hexagonal ReB₂-type OsB₂ ceramic powder was performed by high energy ball milling of elemental Os and B powders. Two different sources of B powder have been used for this mechanochemical synthesis. One B powder consisted of a mixture of amorphous and crystalline phases and a mixture of ¹⁰B and ¹¹B isotopes with a fine particle size, while another B powder was a purely crystalline (rhombohedral) material consisting of enriched ¹¹B isotope with coarse particle size. The same Os powder was used for the synthesis in both cases. It was established that, in the first case, the hexagonal OsB₂ phase was the main product of synthesis with a small quantity of Os₂B₃ phase present after synthesis as an intermediate product. In the second case, where coarse crystalline ¹¹B powder was used as a raw material, only Os₂B₃ boride was synthesized mechanochemically.

The thermal stability of hexagonal OsB₂ powder was studied by heating under argon up to 876 °C and cooling *in vacuo* down to -225 °C. During the heating, the sacrificial reaction $2\text{OsB}_2 + 3\text{O}_2 \rightarrow 2\text{Os} + 2\text{B}_2\text{O}_3$ took place due to presence of O₂/water vapor molecules in the heating chamber, resulting in the oxidation of B atoms and formation of B₂O₃ and precipitation of Os metal out of the OsB₂ lattice. As a result of such phase changes during heating, the lattice parameters of hexagonal OsB₂ changed significantly. The shrinkage of the *a* lattice parameter was recorded in 276-426°C temperature range upon heating, which was attributed to the removal of B atoms from the OsB₂ lattice due to oxidation followed by the precipitation of Os atoms and formation of Os metal. While significant structural changes occurred upon heating due to presence of O₂, the hexagonal OsB₂ ceramic demonstrated good phase stability upon cooling *in vacuo* with linear shrinkage of the lattice parameters and no phase changes detected during cooling.

1. Introduction

The refractory transition metal boride OsB_2 has received special attention due to its ultra-incompressibility and high stiffness arising from a high degree of B-B and Os-B bond covalency [1]. Although three crystal structures, orthorhombic, hexagonal I ReB_2 -type and hexagonal II AlB_2 -type OsB_2 , have been predicted to exist by local density approximations [2], only the thermodynamically stable oP_6 -type OsB_2 $Pmmn$ orthorhombic structure has been experimentally synthesized [3]. Hexagonal ReB_2 -type OsB_2 was reportedly synthesized 50 years ago [4], however the lattice parameters of the phase correspond to those of $\text{OsB}_{1.1}$ (JC-PDS 030-0879 reported in 1978 [5]), suggesting that the phase produced was $\text{OsB}_{1.1}$ and not h - OsB_2 . No other reports on the synthesis of hexagonal OsB_2 structure existed until recently [6, 7], but a number of theoretical predictions have shown that o - OsB_2 can be transformed into hexagonal ReB_2 -type or AlB_2 -type OsB_2 structures upon application of pressure [8, 9]. It was calculated that 2.5 to 10.8 GPa was required to induce the orthorhombic to hexagonal ReB_2 -type OsB_2 phase transformation [8, 9], however these predictions did not specify what type of stress, uniaxial, hydrostatic or shear stress, was used in the calculations. The pressure stability and stress-strain relationship at large structural deformation of orthorhombic OsB_2 has been studied by applying density functional theory [10]. It was shown that the ideal critical stress at which a perfect orthorhombic OsB_2 lattice becomes unstable is equal to 20 GPa in tension but only 9.1 GPa in shear [10], thus indicating that shear stress might play an important role in transforming orthorhombic OsB_2 into hexagonal ReB_2 -type structure. Once formed, hexagonal ReB_2 -type OsB_2 is expected to be a stable phase, as no soft mode at any wave vector of the phonon band structure was found [8]. Experimentally, though, it was shown that orthorhombic OsB_2 exhibits very small volume compressibility with anisotropy present in compressibility of a and c lattice parameters, when the ceramic was subjected to hydrostatic compression up to 34 GPa [3, 11], no phase change was observed.

Recently, a novel high-pressure hexagonal ReB₂-type OsB₂ ceramic powder has been successfully synthesized by high-energy mechanochemical synthesis [6, 7]. It is believed that the high shear stress and strain produced during milling played a major role in the formation of the hexagonal structure. In such synthesis, both elastic and plastic shear deformation facilitated the formation of this new phase by the irreversible $\text{Os} + 2\text{B} \rightarrow h\text{-OsB}_2$ solid-state chemical reaction. During high temperature heating experiments of the *h*-OsB₂ powder in an argon environment, a negative thermal expansion of the hexagonal lattice was observed, where the *a* lattice parameter decreased as temperature increased in 276-426°C temperature range [6]. In addition to the unusual shrinkage, extra diffraction peaks appeared in the high temperature region, which did not belong to the *h*-OsB₂ phase. As a result of such changes, the lattice parameters of *h*-OsB₂ phase changed significantly during heating to 876 °C and cooling back to room temperature. In this work, the thermal stability is studied in greater detail in order to establish the mechanisms driving the lattice contraction and formation of new phases upon heating of hexagonal ReB₂-type OsB₂ ceramic.

2. Experimental

Osmium metal and boron powders were used for the mechanochemical synthesis of OsB₂. Os and B powders with molar ratio of 1:3 were loaded into a tungsten carbide (WC) lined vial (2.25” diameter × 2.5” height) with two 0.5” WC balls. The balls and vial used in the milling were covered with product formed from previous milling syntheses. Information of raw materials and ball milling parameters are shown in Table 1. All loading operations were carried out in an argon-filled glovebox. The vials were sealed with Viton gaskets to reduce oxygen contamination during milling. The milling was performed in a SPEX 8000D mixer mill. Every 30 minutes the milling was interrupted and vials were left for 30 minutes without grinding in order to limit the effects of frictional heating and reduce wear on the mill’s motor. After the *h*-OsB₂ powder was synthesized, a small quantity was loaded into a fused silica

ampule, sealed under vacuum, and annealed up to 6 days at 1050 °C. For the temperature stability experiment, a PANalytical X'Pert Pro MPD system was used to collect X-ray diffraction (XRD) patterns at high temperatures (using an Anton Paar XRK900 reaction chamber) and at low temperatures (using an Oxford PHENiX stage). The OsB₂ sample was protected by flowing pure (99.995%) argon during high temperature (26 °C to 876 °C) XRD experiments and *in vacuo* during low temperature (-225 °C to 25 °C) XRD experiments. Each scan took about 48 minutes and the scans were collected every 50°C both at high and at low temperature. While there was no direct indication of the presence of oxygen in the high temperature chamber during the heating experiments, an air leakage was detected during the XRD measurements on the following day. Therefore, the conditions of the heating OsB₂ experiments cannot preclude the availability of an unspecified amount of oxygen in the Anton Paar XRK900 reaction chamber. Refinement of the structure was performed using the HighScore Plus software. The morphology and particle size of the powders were examined in a Zeiss Merlin scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) detector. A JEOL JEM2200FS aberration-corrected scanning transmission electron microscope (STEM) was used to obtain images of the nanoparticles in all powders.

Table 1. Reaction information and ball milling parameters.

Product	Boron	Osmium	Milling time	Ball to powder mass ratio	Os to B molar ratio
OsB ₂ with ~ 5wt% Os ₂ B ₃	99% pure; mixture of amorphous and crystalline; Alfa Aesar	99.95% pure, Heraeus,	20h	2.7	1:3
Os ₂ B ₃	98% ¹¹ B enriched; crystalline; Ceradyne	99.95% pure, Heraeus,	54h	2.0	1:3

3. Results

3.1. Phase composition of OsB₂ powder after mechanochemical synthesis at room temperature

Room temperature XRD pattern of *h*-OsB₂ collected before heating experiments are shown in Fig. 1A. All peaks found in the diffraction pattern of the powder collected at room temperature before heating were indexed as belonging to hexagonal (*P63/mmc*, 194) OsB₂ with an exception of one low intensity single peak, which was assigned as belonging to the Os₂B₃ phase. The amount of Os₂B₃ phase present was calculated by Rietveld refinement to be equal to about 5 wt% after 20 hours of milling and it was considered as an intermediate product of solid state reaction of OsB₂ formation from Os and B raw powders. The presence of Os₂B₃ compound suggests the following possible route for the synthesis of hexagonal ReB₂-type OsB₂. As Os metal possesses a hexagonal *P63/mmc* crystal lattice [12], it is likely that B atoms diffuse into the lattice filling the interstitial sites to first form osmium monoboride, OsB, then OsB_{1.1}, followed by Os₂B₃, until the hexagonal OsB₂ is finally formed as a major phase. The presence of a small quantity of intermediate Os₂B₃ phase can possibly be explained by the nature of raw B powder used for mechanochemical synthesis of OsB₂. The raw B powder contained a mixture of amorphous and crystalline boron. While amorphous boron is more reactive, the crystalline boron contains icosahedral units with strong covalent bonding between boron atoms which are very difficult to break. The breaking of B-B bonds and forming new B-Os bonds was more favorable in the case of the amorphous material as opposed to the crystalline boron. Therefore, while milling, the amorphous boron readily reacts with Os atoms forming the desired *h*-OsB₂ phase, while crystalline boron only forms the Os₂B₃ phase after 20 hours of milling. As some part of the boron powder existed as a crystalline phase, the formation of OsB₂ compound was less favored, and a small portion of intermediate Os₂B₃ phase was detected after 20 hours of milling. The bright-field STEM and SEM micrographs of hexagonal OsB₂ powder after 20 hours of high energy ball milling are shown in Fig. 1B

and C. The powder consists of small 10-20 nm single crystal nanoparticles (Fig.1B) gathered into larger 2-5 μm agglomerates that can be easily broken apart (Fig. 1C).

Fig. 1: The XRD diffractogram, TEM and SEM images of mechanochemically synthesized OsB_2 (A, B and C) powder at room temperature before heating experiment and Os_2B_3 (D, E and F) produced by ball milling Os and crystalline ^{11}B mixture for 54h.

In order to verify that the hexagonal OsB₂ phase can be formed after high-energy ball milling using only crystalline B as a raw material, crystalline boron powder instead of a mixture of amorphous and crystalline boron was used as a starting material. When crystalline ¹¹B powder was used as one of the constituents of the mechanochemical synthesis (Fig. 2H), the only products (after 54 hours of milling) were a mixture of OsB and Os₂B₃ phases. The X-ray diffraction pattern of the powder synthesized by mechanochemistry with a mixture of OsB and Os₂B₃ phases is shown in Fig. 1D. After synthesis the powder consisted of 2-5 µm agglomerates composed of small 2-5 nm nanoparticles (Figs. 1E and 1F). The lattice parameters and unit cell volume of Os₂B₃ phase synthesized using crystalline ¹¹B powder as a raw material are shown in Table 2.

Table 2. Lattice parameters of Os-B compounds.

	Structure	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	Density (g/cm ³)	Os-Os distance in <i>a-b</i> plane (Å)	Os-Os distance in <i>c</i> direction (Å)
Os	Hexagonal, <i>P63/mmc</i>	2.734	4.3197	27.96	22.580	2.734	2.675
OsB	Hexagonal, <i>P-6m2</i>	2.876	2.868	20.54	17.102	2.876	2.868
Os ₂ B ₃	Hexagonal, <i>P63/mmc</i>	2.908	12.90	94.47	14.501	2.908	2.811 and 3.968
<i>h</i> -OsB ₂	Hexagonal, <i>P63/mmc</i>	2.916	7.376	54.32	12.966	2.916	4.085

The difference in the crystal structure of raw boron powders, such as a mixture of amorphous and rhombohedral crystalline phases of B used for synthesis of OsB₂ and purely rhombohedral crystalline ¹¹B (*R-3m*, No.166) used for synthesis of Os₂B₃ may be only one factor that affects the product composition. Other factors might contribute to the formation of OsB₂ or Os₂B₃ reaction products. As in the first case raw boron powder contained a mixture of ¹⁰B and ¹¹B isotopes, but in the second case enriched ¹¹B isotope was used as a source, the bond strength between B atoms in the two compounds is

Fig. 2: The XRD diffractogram, SEM and bright-field STEM images of osmium metal (A, B and C), amorphous and crystalline boron (D, E and F) and crystalline ^{11}B (G, H and I).

different, because of differences in the mass of the ^{10}B and ^{11}B isotopes, thus different energy would be required to break B-B bonds to form new compounds during mechanochemistry. In addition, while the same Os powder (Fig 2 A-C) was used for synthesis in both cases, the B powders were not only

different isotopes, but also had different particle sizes. While the mixture of amorphous and crystalline B powder consists of relatively small and soft agglomerates with an average particle size of 0.2-1 μm (Fig. 2D-F), the ^{11}B powder consists of large and hard agglomerates with irregular shape, which are difficult to break, with an average particle size of 50-100 μm (Fig. 2G-I). Therefore, not only the stronger crystalline bonds but also the diffusion pathway for mechanochemical formation of OsB_2 is much longer for ^{11}B powder, thus preventing the complete reaction from occurring and allowing only the Os_2B_3 intermediate phase synthesis to complete. It is also important to note that the ratio of the WC balls to the powder under milling was lower in the case where crystalline ^{11}B was used as a source of B in comparison with the synthesis where a mixture of amorphous and crystalline B was used as a raw material. As the ball weight decreases, it contributes to a decrease in the kinetic impact energy that the balls provided to the powder during milling. All of these differences during the synthesis might be contributing factors to the formation of the intermediate product with 1:1.5 Os to B stoichiometry instead of formation of the desired hexagonal OsB_2 in the case when crystalline ^{11}B isotope powder was used as a raw boron source.

3.2. High temperature stability and phase composition of hexagonal OsB_2 under Ar

The 2D XRD contour plot along with XRD patterns of $h\text{-OsB}_2$ collected at selected temperatures upon heating and cooling under argon are presented in Fig. 3. As it was presented in the previous section, the XRD pattern at room temperature contained $h\text{-OsB}_2$ and only a small quantity (~ 5 wt%) of Os_2B_3 intermediate phase. The powder composition was retained upon heating up to 376 $^\circ\text{C}$. However, at 426 $^\circ\text{C}$ small quantities of pure metallic Os started to appear (Fig. 4). Upon further heating, an increasing amount of Os was detected until 726 $^\circ\text{C}$, where it remained almost constant at 26.6 wt% through heating to 876 $^\circ\text{C}$ (Fig. 4). While the Os content increased from 2.0 wt% at 426 $^\circ\text{C}$, when it first was detected by XRD, to 26.6 wt% at 876 $^\circ\text{C}$, the OsB_2 content decreased respectively to 68.3

wt% at 876 °C. The Os_2B_3 phase maintained the same weight percentage (~5 wt%) upon heating and cooling under an argon atmosphere. Once the Os and OsB_2 phases came to some equilibrium at 876 °C, their quantities remained almost constant on cooling with the exception that a small amount of the OsB phase appearing at 826 °C upon cooling (Fig. 4). As one can see from the expanded portion of the XRD contour plot (Fig. 5A), highlighted by a dash line in Fig. 3A, the intensity of the (100) OsB peak can be clearly identified in the XRD pattern (Fig. 5B). For comparison, the pattern collected at 876 °C is also provided (Fig. 5B) where no traces of (100) OsB peak can be detected, Rietveld refinement indicated a 2.3 wt% of OsB present at 826 °C and, once formed, it remained unchanged on cooling to room temperature.

Fig. 3: The *in situ* high temperature XRD contour plot (A) and XRD patterns (B) of *h*-OsB₂ upon heating and cooling under an argon atmosphere.

Fig. 4: The weight percentage of OsB_2 ($\blacklozenge$ or $\diamond$), Os_2B_3 ($\blacksquare$ or $\square$), OsB ($\blacktriangle$ or $\triangle$) and Os ($\bullet$ or $\circ$) as function of temperature upon heating (filled symbol) and cooling (open symbol) under an argon atmosphere.

Fig. 5: An expanded view (A) of the dash-line box in Figure 3A and the corresponding XRD patterns (B) at 876 °C and 826 °C upon cooling.

3.3 Thermochemical expansion of hexagonal OsB₂ upon heating in Ar

The calculated a and c lattice parameters as well as a unit cell volume of h -OsB₂ upon heating and cooling under Ar is shown in Fig. 6. Upon heating, both lattice parameters and unit cell volume of h -OsB₂ increased, as expected due to thermal expansion, however the expansion of the a lattice parameter continued only to 276 °C, where a noticeable shrinkage occurred upon further heating all the way up to 426 °C. While the c lattice parameter of h -OsB₂ did not contract in this temperature range, the slope of its expansion became steeper for the c direction of the lattice starting from 426 °C. The volume of the OsB₂ unit cell decreased in the 326-426 °C temperature range, since the volume is affected by changes both in a and c lattice parameters, such that shrinkage of a lattice parameter contributed to a decrease in the volume of the unit cell. However, above 426 °C both a and c lattice parameters along with unit cell volume showed a significant expansion upon further heating. While the slope of expansion of a lattice parameter was similar in the high temperature 426-876°C range to that at the sub 276°C range, the expansion in c direction was significantly higher above 376°C in comparison with expansion below 376°C. The increase of the a lattice parameter as well as the volume of the unit cell of h -OsB₂ at 426°C coincides with the appearance of pure Os metal detected in the XRD pattern upon heating.

The a and c lattice parameters as well as the unit cell volume of the h -OsB₂ phase decreased upon cooling almost linearly with two different slopes measured both for the a and c lattice parameters (Fig 6ABC). It was found that the a direction of the hexagonal structure shrank faster at higher temperature in comparison with lower temperatures, but the c direction of the lattice shrank slower at higher temperatures range in comparison with lower temperatures. The unit cell volume decreased linearly upon cooling as shrinkages of both a and c lattice parameters contributed uniformly to the volume shrinkage of h -OsB₂.

Fig. 6: The lattice parameters a (A), c (B) and unit cell volume V (C) of OsB₂ together with CTCE of a (D), c (E) and V (F) as function of temperature upon heating (■) and cooling (□) under an argon atmosphere.

The appearance of detectable quantities of pure Os metal began at 426 °C with an increasing amount detected until 726°C where its quantity remained almost constant at ~ 26.6 wt% up to 876 °C. Above 676°C, the Os content was high enough to refine the lattice parameters for the Os phase and the a and c lattice parameters along with the unit cell volume of newly formed h -Os metal are shown in Fig. 7.

Fig. 7: The lattice parameters a (A), c (B) and unit cell volume V (C) of Os as function of temperature upon heating (■) and cooling (□) under an argon atmosphere.

A nearly linear expansion was measured during heating for the a and c lattice parameters along with the volume of h -Os metal, and decreased linearly upon cooling. The difference between coefficients of thermal expansion (CTE) of Os metal upon heating and cooling could possibly be explained by stresses between Os and OsB₂ phases which might appear because of the lattice mismatch between the two phases. The lattice parameters of h -OsB₂ changed dramatically after the other phases formed upon heating and cooling under Ar. The coefficients of thermal expansion of h -Os in a , c and V upon heating and cooling are shown in Table 3. It can be seen in Fig. 6A, B and C, while the a lattice parameter exhibits a thermal shrinkage upon heating, upon cooling it does not exhibit the same behavior, but decreases in an almost linear manner. There is a difference between a values of h -OsB₂ for the material before and after heating with $\Delta a = 6.38 \times 10^{-3} \text{ \AA}$ between the calculations. The c lattice parameter exhibits even more dramatic changes, and while the a lattice parameter becomes smaller after heating/cooling, the c lattice parameter increases by a significant amount. The c lattice parameter does not show a decrease, as it was observed for the a lattice parameter values, but there is a change in the slope for the expansion of c in between 300°C to 400°C temperature range upon heating where at lower temperatures the material expands at a much slower rate in comparison with the expansion above 400°C upon heating. However upon cooling, the thermochemical expansion/shrinkage along c direction is very different from those observed upon heating. The Δc for the lattice parameter measured before and after heating/cooling experiment was equal to $6.06 \times 10^{-2} \text{ \AA}$, which suggests that a significant expansion was observed along the c direction of h -OsB₂ when the phase separation and reduction to Os and osmium monoboride (OsB) occurred. As a result of different shrinkage/expansion behavior of the a and c lattice parameters, the difference in the volume of the unit cell of h -OsB₂ was observed, but the $\Delta V = 0.6145 \text{ \AA}^3$ for the volumes of the material before and after heating was not as large as the difference in the c lattice parameter. The calculated density of h -OsB₂ as a function of temperature is

shown in Fig. 8. Due to negative thermochemical expansion, the density of h -OsB₂ slightly increased in 300-450°C temperature range, but in general at higher temperatures it decreased from 12.97 g/cm³ at room temperature before heating to 12.68 g/cm³ at 876°C. As the lattice parameters of h -OsB₂ changed after cooling, the room temperature density of h -OsB₂ was calculated to be 12.92 g/cm³.

Fig. 8: Density of h -OsB₂ as function of temperature upon heating (■) and cooling (□) under an argon atmosphere.

Table 3. CTEs of Os metal in a , c and V upon heating and cooling under an argon atmosphere.

	CTE of a ($\times 10^{-6}/^{\circ}\text{C}$)	CTE of c ($\times 10^{-6}/^{\circ}\text{C}$)	CTE of V ($\times 10^{-6}/^{\circ}\text{C}$)
Heating	13.52	15.69	43.33
Cooling	6.38	8.59	21.59

Fig. 6D, E, F shows the calculated coefficient of thermochemical expansion (CTCE) upon heating and cooling of h -OsB₂. Indeed, the negative coefficient of thermochemical expansion is observed along the a direction of the lattice upon heating from 276-426 °C. It is also important to note that the

thermochemical contraction of the structure along the c direction of the lattice was much slower at high temperatures than those observed at lower temperatures upon cooling and that is why the CTCE calculated for thermochemical expansion along the c direction is higher at lower (200-300°C) temperatures than those obtained at higher (600-800°C) temperature. The volumetric CTCE did not show negative values, and was rather small in the 276-426°C temperature range with a minimum value of $5.6 \times 10^{-6}/^{\circ}\text{C}$ at 326°C. While CTCEs of OsB₂ measured along the a and c crystallographic directions reached 17 and $23 \times 10^{-6}/^{\circ}\text{C}$ at ~700°C, the volumetric CTCE of the material exhibited much higher values at ~700 °C, with a maximum of $56 \times 10^{-6}/^{\circ}\text{C}$ at 700°C. Such high volumetric expansion upon heating suggests that the practical usage of OsB₂ at high temperature may be limited, as the material might be sensitive to the tensile thermal residual stresses when in contact with other material and also susceptible to crack growth and spontaneous cracking as it should also be very brittle. Once the stoichiometry of OsB came to the equilibrium upon heating, the CTCEs of the resulting phase exhibited much smaller values both for the a and for c lattice parameters along with CTCE of the unit cell volume.

3.4. Low temperature stability of hexagonal OsB₂ *in vacuo*

Although high temperature experiments under an argon atmosphere showed the formation of new phases, such as h -Os and h -OsB, the h -OsB₂ phase remained stable during cooling to -225°C *in vacuo*. The a and c lattice parameters along with the unit cell volume of OsB₂ upon cooling are shown in Fig. 9. A linear dependence can be seen for all three parameters on cooling, The calculations of coefficients of thermal expansion provided almost identical values for the a lattice parameters upon cooling to -225°C and heating back to RT ($\alpha_{a \text{ cool}} = 2.41 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ and $\alpha_{a \text{ heat}} = 2.22 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$), but the values of CTEs along the c direction as well as the unit cell volume of hexagonal lattice have small differences for the cooling and heating parts of the experiment. The CTEs calculated from the

contraction/expansion of the c direction were equal to $\alpha_{c \text{ cool}}=2.99 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ and $\alpha_{c \text{ heat}}=2.86 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ and CTEs calculated from contraction/expansion of the unit cell volume were equal to $\alpha_{V \text{ cool}}=7.82 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ and $\alpha_{V \text{ heat}}=7.30 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$. Similar to the calculations performed for the high temperature experiments, the CTE of the unit cell volume of the $h\text{-OsB}_2$ was significantly higher in comparison with each lattice parameter.

Fig. 9: The lattice parameters a (A), c (B) and the unit cell volume V (C) of $h\text{-OsB}_2$ as function of temperature upon cooling (■) and heating (□) *in vacuo*.

4. Discussion

The cooling, to -225°C *in vacuo*, experiments showed no changes in phase composition or crystal structure of *h*-OsB₂ powder, indicating the stability of the hexagonal ReB₂-type OsB₂ in the low temperature range. The heating experiments of *h*-OsB₂ under Ar indicated that the phase composition changed during heating as pure metallic Os appeared upon heating and OsB formed upon cooling from high temperature (Fig. 4). The appearance of small quantities of pure Os phase upon heating of *h*-OsB₂ can be explained by the presence of small quantities of oxygen in the environment of the heating chamber and the consequent chemical reaction of boron atoms in the *h*-OsB₂ lattice with trace oxygen in the cover gas. The powder produced by ball milling has very high surface area and it is susceptible to oxidation even in the presence of small quantities of oxygen. When a small quantity of O₂ is present, then the following sacrificial reaction can take place where the nanocrystalline and metastable OsB₂ compound is reduced to Os metal and boron oxide, with a possible route for such reduction shown in the Equation (1).

A similar sacrificial reaction was used to produce fine Co particles by oxidizing Co₂B with the formation of Co particles and B₂O₃ [13].

In the reaction between OsB₂ and O₂, it is thermodynamically favorable for oxygen to combine with boron, forming B₂O₃, which is very difficult to detect as the mass absorption coefficient of B₂O₃ is 8.26 cm²/g and it readily forms an amorphous phase, such that small quantities of B₂O₃ are not detectable by powder X-ray diffraction. The disproportionate shrinkage of the *a* lattice parameter upon heating can be explained by the formation of boron oxide in the 276°C - 426°C temperature range by the preferred oxidation of boron atoms in the OsB₂. When boron atoms are removed from the *h*-OsB₂ lattice to form the B₂O₃ phase, boron vacancies are left in the *h*-OsB₂ lattice leading to the shrinkage along the *a*

direction within the 276°C - 426°C temperature range. The confirmation of decreasing of the a lattice parameter in the hexagonal Os-B system as a function of boron stoichiometry is provided in Table 2, where the decrease in the a lattice parameter is reported when the stoichiometry change from 1:2 Os to B in OsB₂, to 1:1.5 Os to B ratio in Os₂B₃, to 1:1 Os to B ratio in OsB to 1:0 Os to B ratio in pure Os metal. Therefore, lattice parameters of OsB₂ are affected by both thermal expansion and by chemical expansion by change in the stoichiometry of the compound and formation of boron vacancies under high temperature. The traces of oxygen or water vapor enabling the changes in the stoichiometry of OsB₂ lead to the formation of OsB_{2-x} compounds, where if $x=0.5$ then Os₂B₃ boride, if $x=1.0$ then OsB monoboride and if $x=2.0$ then pure metallic Os phase will form during the sacrificial chemical reaction between OsB₂ ceramic powder and O₂ molecules. Therefore, it is not that h -OsB₂ has an inherent negative CTE, but instead exhibits changes in the stoichiometry leading to formation of OsB_{2-x} compounds. The c lattice parameter does not show such “negative” thermochemical expansion upon heating. The reason for this could be found upon examination of the ReB₂-type h -OsB₂ lattice [6], which has a layered structure with layers packed along c direction [6] and, therefore, thermal expansion is much larger along the c direction in comparison with the a direction. As thermal expansion plays a significant role in increasing the unit cell parameters of h -OsB₂ upon heating, the c lattice parameter is less affected by removal of B atoms from the lattice in comparison with the much shorter a lattice parameter, where the shrinkage of the bond length is visible and the influence of formation of B vacancies prevails over thermal expansion in a certain temperature range. Upon reaching a critical number of B vacancies due to leaching/removal of B atoms, the hexagonal $P63/mmc$ OsB₂ structure has a significant excess of Os atoms in the lattice which are not bound to B atoms, these Os atoms precipitate out of the h -OsB₂ lattice and a pure metallic Os phase is formed, as detected by XRD starting at 426 °C. As h -Os metal amount increases from 2.0 wt % at 426°C to 26.6 wt % at 776°C, as

the remaining OsB₂ becomes more stoichiometric. Upon further heating from 426°C to 876°C a large expansion of both *a* and *c* lattice parameters was observed. The removal of atoms from *h*-OsB₂ lattice upon heating resulted in very different lattice behavior of the material upon cooling. The shrinkage of the *a* and *c* lattice parameters was observed upon cooling from high temperature to room temperature. The *a* lattice parameter becomes smaller but the *c* lattice parameter of *h*-OsB₂ becomes significantly larger after cooling in comparison to that observed before the heating experiments.

Conclusion

The phase stability and thermal behavior of novel hexagonal ReB₂-type OsB₂ powder was studied in the broad temperature range upon heating up to 876 °C under Ar and cooling to -225°C *in vacuo*. It was found that the *h*-OsB₂ was the major phase in the powder after mechanochemical synthesis with a small quantity (~5 wt%) of *h*-Os₂B₃ also present at room temperature before heating experiments. Os₂B₃ was identified as an intermediate product of mechanochemical synthesis, where presence of crystalline B in the reagent used for mechanochemical synthesis prevented the formation of pure final product *h*-OsB₂ and small quantities of Os₂B₃ compound formed during milling. The formation of Os₂B₃ and OsB phases, but not *h*-OsB₂, was confirmed when coarse crystalline ¹¹B powder was used as a raw B material in high energy ball milling instead of a mixture of amorphous and crystalline B. It was shown that, once synthesized, the *h*-OsB₂ phase was stable upon cooling to -225°C where no structure changes were observed and linear thermal expansion was measured. However, upon heating, the sacrificial chemical reaction between *h*-OsB₂ powder and traces of oxygen and/or water vapor in the heating chamber took place, where B atoms reacted with O₂ molecules leaving the *h*-OsB₂ lattice, forming B₂O₃. This, in turn, lead to the formation of boron vacancies in OsB₂ lattice producing overall B deficiencies and precipitation of a metallic Os phase detectable by X-ray diffraction. Such phase changes lead to the lattice shrinkage and what appeared to be a negative coefficient of thermal

expansion of h -OsB₂ in the a crystallographic direction. As the changes brought to the shrinkage/expansion of the h -OsB₂ lattice were caused not only by the change in the temperature, but also by the change in the stoichiometry of the compound, thus we termed it “thermochemical expansion” to emphasize the effects of both temperature and stoichiometry on the phase changes. In addition, the OsB phase was detected upon cooling of the powder. The phase changes of h -OsB₂ were the reason for the appearance of very different room temperature lattice parameters of h -OsB₂ phase after heating experiments. High values of coefficient of thermochemical expansion of h -OsB₂, especially at 700- 800 °C temperature range, might cause stability and reliability problem for practical applications of this novel material recently synthesized by mechanochemistry.

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