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Phase relations in boron at pressures up to 18 GPa and temperatures up to 2200 °C

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The phase relations in boron have been investigated at high pressure and high temperature using a multianvil apparatus, and the quenched sample has been analyzed by x-ray diffraction, Raman spectra, and transmission electron microscopy. We demonstrate that γ-B_{28} can be synthesized over a wide pressure and temperature range, and α-tetragonal B_{50} (T-B_{50}) is obtained at higher temperatures and similar pressures. The phase boundary of the β-B_{106}, γ-B_{28}, and T-B_{50} is determined at pressures between 7.0 and 18 GPa and the temperatures of 500–2200 °C. The results suggest that T-B_{50} might be an intermediate phase formed for kinetic reasons (Ostwald rule) on the way from β-B_{106} to β-tetragonal B_{192} (T-192) and γ-B_{28} to T-192.

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I. INTRODUCTION

Boron has been widely studied because of its complex polymorphism and fascinating chemical and physical properties.[1–13] All known structures of boron and some boron-rich compounds contain B_{12} icosahedron, which can be flexibly linked into rigid framework structures. Many previous studies of boron concentrated on the synthesis and structural characterization of pure forms. Now, probably four of the reported boron phases correspond to the pure element[1,2,5,14–17]: α-rhombohedral B_{12} (α-B_{12}), β-rhombohedral B_{106} (β-B_{106}), β-tetragonal B_{192} (T-192), and γ-B_{28}, but α-tetragonal B_{50} (T-B_{50} or T-B_{52}) are also believed to exist,[18] and the single-crystal T-B_{50} crystal was obtained by Laubengayer *et al.*[19] (The crystal structure of T-B_{50} was proposed by Hoard *et al.*[20,21] [P42/nnm (134), $a = 8.75$ Å and $c = 5.06$ Å]). Recently, Ekimov and Zibrov[22] and Kurakevych *et al.*[23] also reported that T-B_{50} was synthesized at high pressure and high temperature (HPHT). In previous studies, Oganov *et al.*[1] gave a phase diagram of boron based on their work and previous experiments[5,8,24] and theoretical studies.[25] Shirai *et al.*[7,26,27] studied the properties of β-B_{106} and the phase diagram of β-B_{106} and α-B_{12}. By *ab initio* calculations, they found that at zero temperature α-B_{12} is more stable than β-B_{106}. However, scientists still do not definitively know which of these two forms is the stable form. In the experiments, Zarechnaya *et al.*[2] reported a tentative phase boundary between β-B_{106} and γ-B_{28} based on the results of two multianvil quenched experiments and some diamond anvil cell (DAC) experiments. Parakhonskiy *et al.*[3] also reported the phase relations of α-B_{12}, β-B_{106}, and γ-B_{28}. However, they did not see the stability of the T-192 and/or T-B_{50} phase, and they synthesized α-B_{12} and γ-B_{28} in liquid metal (Pt and Au capsule might melt at their HPHT conditions). Liquid metal might act as the solvent and make the phase transition easier. Thus, the relative stability of boron phases is still experimentally unresolved at HPHT. The main reason might mainly be ascribed to the complexity of the boron crystal structures themselves.

II. EXPERIMENTAL DETAILS

In this paper, we conducted a series of experiments on the HPHT synthesis of γ-B_{28} and T-B_{50} from β-B_{106} (claimed purity 99.6%, Goodfellow) and examined β-B_{106} at HPHT using a multianvil press (see supplementary material[28]), and quenched the sample to ambient conditions for x-ray diffraction (XRD) and Raman spectra to investigate the phase relations of β-B_{106}, γ-B_{28}, and T-B_{50}. Table I shows the HPHT experiments on boron. The T-B_{50} samples were also loaded into a focused ion beam (FIB) system (JOEL JEM-9310FIB) to prepare transmission electron microscopy (TEM) foils. The detailed procedure of FIB milling for TEM foil preparation is described elsewhere.[29] TEM observations were carried out using a JEOL JEM-2010, operated at 200 kV. Selected area electron diffraction (SAED) was employed to characterize T-B_{50}.

III. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns and Raman spectra of the recovered products that were heated at 1600 °C for 2 h at 15 GPa and the starting materials. From the XRD patterns [Fig. 1(a)], we find that γ-B_{28} is synthesized under this HPHT condition. Besides the γ-B_{28}, further phase identification shows that the HPHT quenched sample also contain small amounts of MgO (MgO capsule). Additionally, the XRD data of γ-boron from Oganov *et al.*[1] are also shown in Fig. 1(a), and we can find that our XRD patterns are in good agreement with the reported results. The recovered samples were also investigated using Raman spectra. The Raman spectra of the recovered sample are also different from β-B_{106} [Fig. 1(b)], but are similar to that of γ-B_{28} reported.[2,30] Therefore, we confirm that γ-B_{28} is successfully synthesized under this HPHT condition. In addition, we also tried to synthesize γ-B_{28} under different HPHT conditions (Table I). XRD and Raman spectra results indicate that γ-B_{28} can also be synthesized at 13 GPa and high temperatures of 1300 °C and 1600 °C for 2 h, 10 min, and even for just 1 min; 15 GPa and 1800 °C for 10 min; and 18 GPa and 2000 °C for 10 min. The results demonstrate that the γ-B_{28} can be synthesized over a wide pressure and temperature (P-T) range. By indexing the powder XRD data using Powder X,[31] the structure of quenched samples was solved to be an orthorhombic unit cell **(**$a = 5.0570(6)$ Å, $b = 5.6165(7)$ Å, $c = 6.9815(9)$ Å, $V = 198.29(6)$ Å^3**)**. Our results are comparable to previous experimental ($a = 5.0544$ Å, $b = 5.6199$ Å, $c = 6.9873$ Å and $a = 5.0576$ Å, $b = 5.6245$ Å, $c = 6.9884$ Å) and theoretical results.[1,4,32,33]

TABLE I. Summary of experimental conditions and results.

	Conditions				
Experiment no.	T (°C)	P (GPa)	Capsule	Heating time	Phase identified
OD828	1000	8.0	MgO	2 h	β
OS2036	1000	8.5	MgO	4 h	β
OS2039	1000	9.0	hBN	4 h	β and γ
OD817	1000	10	MgO	30 min	β and γ
OD876	1000	13	hBN	2 h	β and γ
OS2029	1300	8.5	MgO	2 h	β
OS2028	1300	9.0	MgO	2 h	β and γ
OS2025	1300	9.5	MgO	2 h	β and γ
OD831	1300	10	MgO	2 h	β and γ
OD874	1300	13	hBN	10 min	γ
OS2043	1500	9.0	MgO/BN	2 h	β and γ
OS2027	1600	9.0	MgO/BN	30 min	β
OD860	1600	9.5	MgO	2 h	β and γ
OS2016	1600	10	MgO	2 h	β and γ
OD812	1600	15	MgO	30 min	γ
OD871	1600	13	hBN	2 h	γ
OD872	1600	13	hBN	10 min	γ
OD935	1600	13	Pt	1 min	γ
OD918	1800	15	Pt	10 min	γ
OD895	2000	18	hBN	10 min	γ
OD920	900	9.0	Au/Pt	20 h	β
OD922	900	9.5	Au/Pt	20 h	β
OD928	850	13	Au	24 h	β and γ
OD930	500	13	Au	24 h	β
OD933	700	13	Au	24 h	β
OD976	1800	12	Al_2O_3	30 min	γ
OD975	2000	12	Al_2O_3	5 min	$\gamma + \text{T-B}_{50}$
OD942	2100	15	Ta	5 min	$\gamma + \text{T-B}_{50}$
OD891	2200	18	hBN	2 min	$\gamma + \text{T-B}_{50}$
OD994	2000	7.0	Al_2O_3	5 min	β
OD999	2000	8.0	Al_2O_3	5 min	β
OD997	2000	9.5	Al_2O_3	5 min	$\beta + \text{T-B}_{50}$
OD1001	2000	9.0	Al_2O_3	5 min	$\beta + \text{T-B}_{50}$
OD1003	1700	9.5	Al_2O_3	15 min	β and γ
OD1008	1800	9.0	Al_2O_3	5 min	β
OD1009 (γ + T)[a]	1600	12.	Al_2O_3	50 min	γ
OD1011 (γ)[b]	1700	7.0	Al_2O_3	20 min	β
OD1013 (β + T)[c]	1700	7.0	Al_2O_3	20 min	β

[a] $\gamma + \text{T-B}_{50}$ starting materials.
[b] γ-boron starting material.
[c] $\beta + \text{T-B}_{50}$ starting materials.

T-B_{50} is also based on B_{12} icosahedra, Kurakevych *et al.*[23] observed the crystallization of tetragonal boron T-B_{50} phase as an intermediate one (from β-B_{106} to γ-B_{28}) at HPHT. In our experiment, we studied β-B_{106} at 2000 °C and high pressures of 9.5 and 12 GPa, and the quenched sample is pure boron using energy-dispersive x-ray spectroscopy analysis (see supplementary material, figure S1[28]). Figure 2(a) shows the Raman spectra of the recovered products that were heated at 2000 °C for 5 min at 12 GPa and β-B_{106}. Because boron is a light element and poor x-ray scatterer, we did not obtain good-quality XRD patterns. However, the phase transition of boron is easy to clarify in Raman spectra, in which we can find color zones different from the optical image [Fig. 2(b)]. Raman spectra show that light gray and gray zones correspond to γ-B_{28}, but Raman spectra of dark gray are different from the β-B_{106}, α-B_{12},[4] and γ-B_{28}. The same results were obtained at 15 GPa and 2100 °C and 18 GPa and 2200 °C. Additionally, we conducted β-B_{106} at 9.5 GPa and a similar temperature and quenched the sample to ambient conditions for Raman spectra. Some special grains appear in the sample from the microscopic image [Fig. 2(c)], and Raman spectra of these grains are the same as the dark gray of the quenched sample under higher pressure; the other area is β-B_{106}. As the XRD quality is very low, and it is difficult to identify phase. We prepared TEM foils [dark gray zone in Fig. 2(b)] using the FIB system for TEM observations. Figures 2(d) and 2(e) shows the TEM image and SAED patterns of TEM foils. The SAED patterns can be indexed as the diffraction patterns of the [1-10] zone axis of

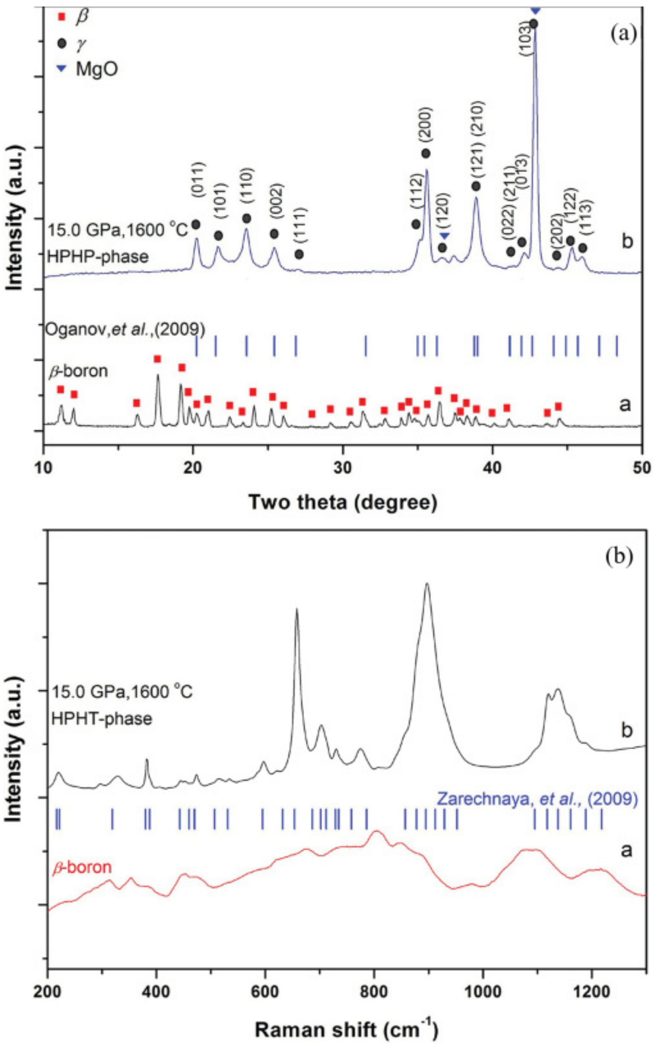

FIG. 1. (Color online) XRD patterns (a) and Raman spectra (b) of β-B_{106} treated at 15 GPa and 1600 °C and β-B_{106} and compared with previous experimental results from Oganov *et al.* (Ref. 1) and Zarechnaya *et al.* (Refs. 4 and 30).

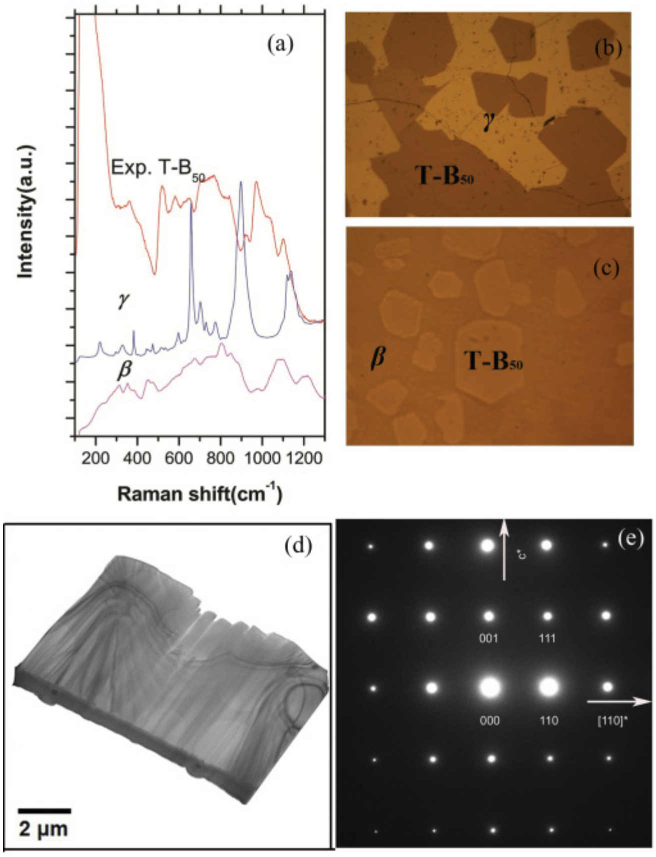

FIG. 2. (Color online) (a) Raman spectra of T-B_{50} synthesized at 2000 °C and high pressures of 9.5 and 12 GPa compared with Raman spectra of β-B_{106} and γ-B_{28}. (b) Optical photo of quenched sample at 12 GPa. (c) Optical photo of quenched sample at 9.5 GPa. (d) TEM image of the single-crystal foil. (e) SAED pattern shows the diffraction patterns of the [1-10] zone axis of T-B_{50}.

T-B_{50}, and the lattice parameters are $a = 8.71$ Å and $c = 5.00$ Å, which is in good agreement with the reference ($a = 8.73$ Å, $c = 5.03$ Å[19] and $a = 8.75$ Å, $c = 5.06$ Å[20,21]). Thus, we have observed the T-B_{50} from β-B_{106} at HPHT and presented the Raman spectra of T-B_{50}. Our results also suggest the T-B_{50} is a pure boron phase and can be synthesized at HPHT.

To understand the relative phase stability of boron, we investigated the phase relations of γ-B_{28}, β-B_{106}, and T-B_{50}. Table I shows the experimental synthesis conditions and the characterization of the recovered samples, and Fig. 3 shows selected XRD patterns and Raman spectra of the quenched samples from HPHT conditions. Characteristic x-ray and Raman spectra of the starting material, β-B_{106}, are also presented in the bottom curves (*a* in Fig. 3). At high temperatures of 1300 °C, it has a similar XRD pattern [curve *b*, Fig. 3(a)] to that of β-B_{106}, and no phase transitions are detected at 8.5 GPa. At 9.0 GPa, we find that the peaks of γ-B_{28} appear [curve *c*, Fig. 3(a)]. The peaks of β-B_{106} decrease with increasing pressure. When pressure increases up to 10 GPa, the diffraction pattern shows γ-boron and the peaks of β-B_{106} almost disappear [curve *d*, Fig. 3(a)]. Raman spectra also demonstrate a drastic change. The Raman spectra of starting materials and quenched sample from 8.5 GPa and 1300 °C [curves *a* and *b*, Fig. 3(b)] are dominated by the β-B_{106} phonon modes, whereas the spectra of 9.0 GPa or higher [curves *c*, *d*, and *e*; Fig. 3(b)] significantly differ from the previous two. Based on the XRD results and Raman spectra, we confirm the phase transition from β-B_{106} to γ-B_{28} between 8.5 GPa and 9.0 GPa below 1300 °C.

Samples treated to temperatures of 1000 °C and 1600 °C at different pressures were also investigated using XRD and Raman spectra. The samples usually underwent HPHT conditions for 2 h, although some samples were treated for 4 h or more than 20 h under P-T conditions near the phase boundary and at a relatively lower temperature. A combination of the XRD and Raman spectra results (Table I) [also see supplementary material, fig. S2(a)–(d)[28]] reveals that the P-T conditions of the β-B_{106} to γ-B_{28} phase transition lie between 8.5 and 9.0 GPa and between 9.0 and 9.5 GPa under high temperatures of 1000 and 1600 °C, respectively.

To further understand the phase boundary of β-B_{106} to T-B_{50} and γ-B_{28} to T-B_{50}, we conducted β-B_{106} experiments at pressures between 7.0 and 18 GPa and temperatures of

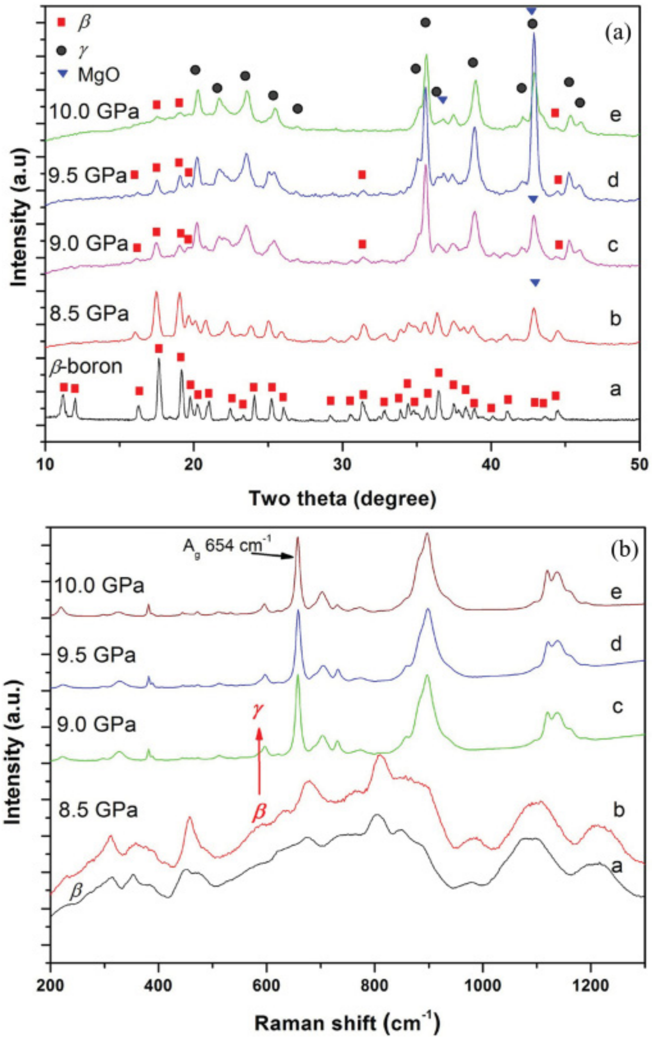

FIG. 3. (Color online) XRD patterns and Raman spectra of β-boron treated at HPHT and β-B_{106}. (a) XRD patterns, (b) Raman spectra.

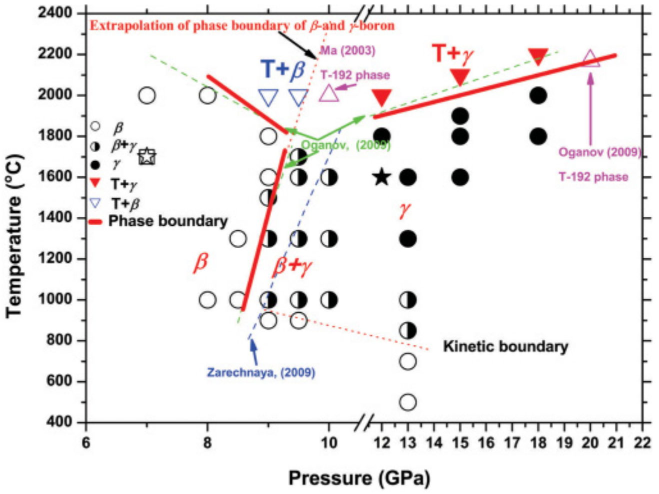

FIG. 4. (Color online) Phase relations of β-B_{106} (open circles), γ-B_{28} (solid circles), and T-B_{50}. The semisolid circles represent β-B_{106} and γ-B_{28} in coexistence, the open and solid inverse triangles are β-B_{106} and T-B_{50} mixtures, and γ-B_{28} and T-B_{50} mixtures, respectively, and the triangles represent P-T conditions of the T-192 phase from Oganov *et al.* (Ref. 1) and Ma *et al.* (Ref. 5), respectively. The line is the phase boundary of β-B_{106}, γ-B_{28}, and T-192 boron, and the inset show the theoretical phase boundary from Oganov *et al.* (Ref. 1) and the tentative phase boundary from Zarechnaya *et al.* (Ref. 2). Reverse experiments are also shown in this figure; square is phase transition from γ-B_{28} to β-B_{106}, open and solid stars present T-B_{50} transformations back to β-B_{106} and γ-B_{28}, respectively.

1700–2200 °C, and we quenched the samples to ambient conditions for XRD and Raman spectra (Table I). Under high pressures of 12, 15, and 18 GPa, when β-B_{106} is heated up to 1800, 1900, and 2000 °C, respectively, XRD and Raman spectra indicate that pure γ-B_{28} is successfully synthesized. At similar pressures, the T-B_{50} is produced at higher temperatures of 2000–2200 °C (Table I). However, it is difficult to synthesize pure T-B_{50} according to our experimental results. Under lower pressures of 7.0 and 8.0 GPa and high temperature of 2000 °C, the quenched sample is pure β-B_{106} from XRD and Raman spectra. When we increase the pressure to 9.0 GPa, β-B_{106} and T-B_{50} coexist in the quenched sample at the high temperature of 2000 °C, but it is pure β-B_{106} at 1800 °C. Thus, we give a tentative phase boundary of γ-B_{28} to T-B_{50} and β-B_{106} to T-B_{50} according to our experimental results (Fig. 4).

Figure 4 shows the P-T region of the phase relations of β-B_{106}, γ-B_{28}, and T-B_{50} compared with the results of Oganov *et al.*[1] and Zarechnaya *et al.*[2], and the inset shows the P-T conditions for synthesis of the T-192 phase from Oganov *et al.*[1] and Ma *et al.*[5] In this P-T region, our β-B_{106} to γ-B_{28} phase boundary is in good agreement with Oganov's theoretical results and Zarechnaya's DAC results. Our results indicate that the phase relations of β-B_{106} and γ-B_{28} have almost no pressure dependence. The other two phase boundaries (β-B_{106}/T-B_{50} and γ-B_{28}/T-B_{50}) have not been reported so far on the basis of experimental data and prove that the T-B_{50} phase is not only a pure boron phase but has a field of stability at high pressures and temperatures.

By extrapolation of the β-B_{106} and γ-B_{28} phase boundary, we find β + T-B_{50} is in the "phase stability" of β-B_{106}, and γ + T-B_{50} is in the phase stability of γ-B_{28}. This is why we synthesize a mixture of β-B_{106} and T-B_{50} at a lower pressure and a mixture of γ-B_{28} and T-B_{50} at a higher pressure. Additionally, we also examined γ-B_{28}, a mixture of γ-B_{28} and T-B_{50}, and a mixture of β-B_{106} and T-B_{50} at 7.0 GPa and 1700 °C, 12 GPa and 1600 °C, and 7.0 GPa and 1700 °C, respectively. XRD and Raman spectra results show that γ-B_{28} and T-B_{50} transform back to β-B_{106} and T-B_{50} transforms back to γ-B_{28} under the stability field of β-B_{106} and γ-B_{28}, respectively. Combined with the previous results[1,2,5] and our study, we find that β-B_{106} transforms into γ-B_{28} at high pressure and certain temperatures and then transforms back to β-B_{106} at relatively low pressures (~9 GPa). With increasing temperature up to 2000 °C, β-B_{106} will transform to T-B_{50}; however, β-B_{106} transforms into γ-B_{28} and then transforms into T-B_{50} at relatively higher pressures (more than ~10 GPa). These results show that γ-B_{28} is stable phase under a certain pressures (above ~9 GPa) in good agreement with previous theoretical results.[1] However, we did not observe the T-192 phase in our experiment. The phase stability of T-B_{50} is in the theoretical phase stability of the T-192 phase, and Kurakevych *et al.*[23] also found crystallization of the T-B_{50} phase to be intermediate (between β-B_{106} and γ-B_{28}), so we suggest T-B_{50} could exist as an intermediate phase (along the phase boundary of the γ-B_{28} to T-192 phase and the β-B_{106} to T-192 phase from Oganov *et al.*[1] results). These results might indicate the reason behind the Ostwald rule of stages,[34,35] which shows the possible phases, with intermediate values, of free Gibbs energy before the system has transformed into the thermodynamically stable phase with the most stable crystal structure. According to first principles calculations,[1] the T-192 phase should be stable in our experimental conditions. From the phase diagram, our experiments reveal that T-B_{50} exists along the phase boundary of the γ-B_{28} to T-192 phase and β-B_{106} to T-192 phase.[1] The difference could be explained by the non-negligible 0 K configurational entropy of T-192 and T-B_{50}, which strongly decreases the free enthalpy at high temperatures. In our experimental conditions, the configurational entropy of T-192 should be greater than T-B_{50}, which is why we obtained just the T-B_{50}. If we continue heating to higher temperatures, the configurational entropy of T-192 will be less than T-B_{50}, and the system will transform into the thermodynamically stable phase with the most stable crystal structure (T-192). Thus, more experimental and theoretical studies on structural and phase stability of boron are strongly recommended, especially the thermodynamic phase relations between T-B_{192} and T-B_{50} at HPHT. Here, we also give the kinetic boundary of β-B_{106} to γ-B_{28}. The results indicate that kinetic barriers decrease with increasing pressure, and no α-B_{12} was found in our HPHT conditions.

IV. CONCLUSION

We synthesized γ-B_{28} and T-B_{50} from β-B_{106} under HPHT using a multianvil press and investigated the phase relations of β-B_{106}, γ-B_{28}, and T-B_{50}. We demonstrate that γ-B_{28} can be synthesized over a wide P-T range and that T-B_{50} is obtained at higher temperatures and similar pressures, and we suggest that T-B_{50} might be an intermediate phase formed for kinetic reasons (Ostwald rule) on the way from β-B_{106} to T-192 and γ-B_{28} to T-192.

On the basis of the XRD, Raman spectra, and TEM results, we present the experimental phase relations in boron at pressures up to 18 GPa and temperatures up to 2200 °C. We suggest that β-B_{106} and γ-B_{28} transform directly to T-B_{50} at lower and higher pressure, respectively. Additionally, T-B_{50} transforms back to β-B_{106} and γ-B_{28} during quenching under lower pressures and higher pressures, respectively. The results provide fundamental information for better understanding of the phase diagram of this interesting material. However, more experimental and theoretical studies on structural and mechanical properties are strongly recommended.

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