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Article

Thermodynamic Analysis of the V-Shaped Area of High Pressure and High Temperature in Cubic Boron Nitride Synthesis with Li_3N as a Catalyst

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Abstract: The possibilities of different phase transitions to cBN with Li_3N as catalyst at high temperature and high pressure (1600–2200 K, 4.8–6.0 GPa) are analyzed, in the framework of the second law of thermodynamics. The Gibbs free energy (ΔG) of three reactions which may happen in the Li_3N-BN system: hBN + $Li_3N \rightarrow Li_3BN_2$, hBN→cBN, and $Li_3BN_2 \rightarrow$ cBN + Li_3N, is calculated, with the influence of high temperature and high pressure on volume included. We show that ΔG of hBN + $Li_3N \rightarrow Li_3BN_2$ and hBN→cBN are between −35~−10 KJ·mol^{-1} and −25~−19 KJ·mol^{-1}, respectively. However, ΔG of $Li_3BN_2 \rightarrow$ cBN + Li_3N can be positive or negative. The area formed by the positive data is a V-shaped area, which covers the most part of the cBN growing V-shaped area. It confirms that Li_3BN_2 is stable in the P-T area of cBN synthesis, and cBN is probably transformed directly from hBN. Analysis suggests that Li_3BN_2 promotes the transition from hBN to cBN.

Keywords: cBN single crystal; high pressure and high temperature; V-shaped area; thermodynamic analysis; Gibbs free energy

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1. Introduction

High static pressure is the most common method to synthesize cubic boron nitride (cBN) with hexagonal boron nitride (hBN) as raw material and with alkaline metals or alkaline-earth metals and their nitrides as catalysts. The cBN synthesized with lithium nitride (Li_3N) is widely used because of its regular crystal shape and suitable particle size. A layer of white powder covers the surface of cBN crystal during the growth. Phase structure characterizations show that the layer is composed of hBN, micro cBN and lithium boron nitrides (Li_3BN_2) [1]. It is very desirable to study their relationships to understand the phase transition mechanism of cBN as they are in direct contact with the cBN single crystals.

Previous studies indicate that no matter what kind of catalyst is adopted, the temperature and pressure forms a V-shaped area [2–4] where cBN can grow stably. Besides there is a short-range ordered or medium-range ordered structure in high temperature and high pressure (HPHT) system [5], namely a solid microstructure existing in the HPHT system. It was proposed that cBN was directly transformed from hBN [6], while [7] believed that cBN was precipitated from solvent. Thermodynamic analysis plays an important role in understanding the synthesis mechanism of diamond [8,9]. Therefore it is possible to investigate the phase transition mechanism of cBN because of the similar structure. However, there are few reports about the thermodynamics of the cBN transition mechanism with catalyst at HPHT due to the absence of thermodynamic data at HPHT and the ambiguity of the mechanism. Bocquillon *et al*. [3,10] put forward the following reactions in the Li_3N-hBN system:

$$Li_3N + hBN \rightarrow Li_3BN_2 \tag{1}$$

$$Li_3BN_2 \rightarrow Li_3N + cBN \tag{2}$$

After the reactions, all of the phase are found around the cBN crystals by XRD [1], except for the volatile Li_3N. It is difficult to identify the reactions through experiments because the online inspection is impractical. The synthesis of cBN is an isobaric and isothermal process, and we can apply classical thermodynamics to analyze the reactions in the system by querying the related thermodynamic data. Based on the second law of thermodynamics, we calculate the change of Gibbs free energy in (1) and (2) and analyze the thermodynamic transformation of cBN in V-shaped area of the system.

2. Calculation

The calculation is based on the second law of thermodynamics. The change of Gibbs free energy ΔG is:

$$G_T^P = G_T^P + \int_{P^\theta}^{P} VdP \tag{3}$$

Under the isobaric condition, ΔG can be obtained:

$$\Delta G_T^\theta = \Delta H_T^\theta - T\Delta S_T^\theta = \Delta_f H^\theta + \int_{T_0}^{T} \Delta C_P dT - T \times (\Delta_r S^\theta + \int_{T_0}^{T} \frac{\Delta C_P}{T} dT) \tag{4}$$

ΔG between different temperatures and pressures can be expressed as [11]:

$$\begin{aligned} \Delta G_T^P &= (\Delta H_T^0 - T\Delta S_T^0) + (\int_{T_0}^{T} \Delta C_P - T\int_{T0}^{T} \frac{\Delta C_P}{T} dT) + \\ &+ \int_{P0}^{P} [(V_0 + \Delta V_T + \Delta V_P)_{\text{Product}} - (V_0 + \Delta V_T + \Delta V_P)_{\text{Reactant}}] dP \end{aligned} \tag{5}$$

Equation (5) takes the influence of temperature and pressure to volume into consideration. ΔH_T^0 and ΔS_T^0 are enthalpy and entropy of crystalline phase in the system, respectively. V_0 is the mole volume at normal temperature and pressure. ΔV_T and ΔV_P are the variation of mole volume with constant temperature and pressure, respectively. According to [12,13], the related thermodynamic quantities can be acquired. Similarly, we get ΔG of Li_3BN_2 from [14]:

$$\Delta G^{\theta}(T,P^{\theta}) = -425.42206 + 0.07512T - 1.778\times10^{-4}T^2 + \\ + 4.144\times10^{-8}T^3 + \frac{27.9}{T} - 9.306\times10^{-3}T\ln T \tag{6}$$

298 K is chosen as the start temperature. ΔV_T and ΔV_P are calculated in the following.

2.1. ΔV_P

Based on the state equation of crystal under high pressure by Sung [15], we use the Birch-Murnaghan equation of crystal state to calculate the variation of volume under high pressure:

$$P = \frac{3}{2}\left(\frac{V_0}{V_0+\Delta V_P}\right)^{\frac{5}{3}}\left[\left(\frac{V_0}{V_0+\Delta V_P}\right)^{\frac{2}{3}}-1\right]\left\{1+\frac{3}{4}(B_0^{'}-4)\left[\left(\frac{V_0}{V_0+\Delta V_P}\right)^{\frac{2}{3}}-1\right]\right\} \tag{7}$$

In Equation (7), B_0 is bulk modulus, and B_0' is the first derivative of the pressure with respect to bulk modulus. From Equation (7), the relation between ΔV_P and pressure can be obtained. Table 1 shows the physical parameters of materials in reactions in the Li_3N-BN HPHT system.

Table 1. Physical parameters of the materials participating in the reactions.

Material	V_0/cm^3·mol^{-1}	B_0/GPa	B_0'/GPa
cBN	7.1150	398.6 [16]	3.85 [16]
hBN	10.8820	36.7 [17]	5.6 [17]
Li_3N	27.2031	98 [18]	4.04 [18]
Li_3BN_2	34.0850	-	-

In Table 1, the B_0 and B_0' are not found in references. According to [11], they can be deduced from Vegard's law from the B_0 and B_0' of Li_3N and cBN:

$$B_0 = x_1B_1 + x_2B_2 = B_{Li_3N} + B_{cBN} \tag{8}$$

In Equation (8), B_0 and B_1 and B_2 are the bulk modulus of Li_3BN_2, Li_3N and cBN, respectively. x_1, x_2 are the percentage of Li_3N and cBN, with $x_2 = 1 - x_1$. B_0' could be calculated by the same method. The B_0 of Li_3BN_2 is 248.3 and B_0' is 3.945.

2.2. ΔV_T

ΔV_T can be obtained on the basis of the thermal expansion properties of crystals:.

$$\Delta V_T = V_0\beta\Delta T = V_0\beta(T-T_0) \tag{9}$$

In Equation (9), β refers to the volume expansion coefficient, and its value of hBN, cBN and Li_3N can be obtained from [19,20], but there has been no report on the value β of Li_3BN_2. It can be calculated as follows:

$$C_p - C_v = \frac{V_0 T \beta^2}{\kappa} \tag{10}$$

where C_v is the molar heat capacity at constant volume and κ is the isothermal compressibility with $\kappa = 1/B$. According to the definition of bulk modulus, the Equation (10) can be written as

$$C_P - C_V = (B_0 + B_0^{'} \times P) V_0 T \beta^2 \tag{11}$$

From [14] C_p of Li_3BN_2 can be obtained as follows:

$$C_P = 9.306 + 355.6 \times 10^{-3} T - 5.58 \times 10^4 T^{-2} - 24.86 \times 10^{-5} T^2 \tag{12}$$

and the β of Li_3BN_2 can thus be calculated:

$$\beta = 1.68324 \times 10^{-4} + 1.21253 \times 10^{-8} T - 8.96867 \times 10^{-11} T^2 + 1.30857 \times 10^{-14} T^3 \tag{13}$$

3. Results and Discussion

Different P-T areas of cBN growth in the Li_3N-hBN system [2–4] have been proposed, which may be related to the purity and degree of order of the hBN and the synthesis process used. The lowest synthesis pressure is 4.8 GPa and the minimum synthesis temperature is 1690 K at 5.0 GPa in Li_3N-hBN system [4], which approximates the V-shaped area proposed in [3]. Ko [7] found that the lowest temperature was 1620 K at 5.3 GPa, lower than the lowest temperature (1723 K) reported by Bocquillon [3]. Considering the industrial application and the reliability of the numerical calculation is performed in an expanded region of 1600–2200 K and 4.8–6.0 GPa.

Table 2 shows the change of Gibbs free energy of Li_3N + hBN→Li_3BN_2 in the HPHT area (1600–2200 K, 4.8–6.0 GPa) of cBN synthesis in the Li_3N-hBN system. The values of ΔG are between −35 and −10 KJ·mol^{-1}. This illustrates that Li_3N can transform into Li_3BN_2 in this P-T area, in coincidence with the XRD results of the catalyst after synthesis [1].

Table 2. ΔG of hBN + Li_3N→Li_3BN_2 at different temperatures and pressures.

T/K	ΔG/(KJ·mol^{-1})						
	4.8 GPa	**5.0 GPa**	**5.2 GPa**	**5.4 GPa**	**5.6 GPa**	**5.8 GPa**	**6.0 GPa**
1600	−16.4319	−17.9111	−19.3804	−20.8399	−22.2898	−23.7301	−25.1611
1650	−17.3670	−18.9879	−20.5988	−22.2000	−23.7916	−25.3736	−26.9463
1700	−18.1161	−19.8872	−21.6483	−23.3996	−25.1413	−26.8735	−28.5963
1750	−18.6561	−20.5857	−22.5054	−24.4154	−26.3156	−28.2064	−30.0878
1800	−18.9630	−21.0597	−23.1464	−25.2233	−27.2905	−29.3483	−31.3967
1850	−19.0122	−21.2842	−23.5463	−25.7985	−28.0411	−30.2743	−32.4980
1900	−18.7784	−21.2340	−23.6797	−26.1156	−28.5418	−30.9586	−33.3660
1950	−18.2357	−20.8831	−23.5206	−26.1482	−28.7663	−31.3749	−33.9740
2000	−17.3573	−20.2046	−23.0420	−25.8696	−28.6875	−31.4959	−34.2951
2050	−16.1162	−19.1714	−22.2166	−25.2521	−28.2779	−31.2942	−34.3011
2100	−14.4845	−17.7554	−21.0163	−24.2674	−27.5089	−30.7409	−33.9634
2150	−12.4339	−15.9281	−19.4124	−22.8869	−26.3518	−29.8071	−33.2531
2200	−9.9353	−13.6604	−17.3756	−21.0809	−24.7767	−28.4629	−32.1398

ΔG varies regularly with the increase of temperature and pressure. It decreases firstly and then rises with the increasing temperature under constant pressure. ΔG decreases monotonically with the increasing pressure when temperature keeps constant. The higher temperature and pressure, the more negative ΔG, it is easier to generate Li_3BN_2.The possibility of the reaction exists, although the absolute value of ΔG is very small.

Table 3 shows ΔG of transition hBN-cBN in HPHT area (1600–2200 K, 4.8–6.0 GPa) of cBN synthesis. In consideration of the influence of temperature and pressure on phase volume, relatively precise calculation results are obtained. ΔG of the transition is between −25 and −19 KJ·mol^{-1}. ΔG is negative and its absolute value increases with the increasing temperature and pressure, and it is more and more probable for the transition to occur. From Table 3, we find that ΔG changes more sharply with the pressure than with the temperature. Therefore, the transition of hBN to cBN is probable in the P-T area, and pressure is greater impact than temperature.

Table 3. ΔG of hBN→cBN at different temperatures and pressures.

T/K	ΔG/(KJ·mol^{-1})						
	4.8 GPa	**5.0 GPa**	**5.2 GPa**	**5.4 GPa**	**5.6 GPa**	**5.8 GPa**	**6.0 GPa**
1600	−19.7724	−20.4187	−21.0596	−21.6952	−22.3255	−22.9507	−23.5707
1650	−19.7917	−20.4391	−21.0810	−21.7176	−22.3490	−22.9752	−23.5963
1700	−19.8295	−20.4774	−21.1198	−21.7569	−22.3887	−23.0154	−23.6370
1750	−19.8857	−20.5334	−21.1758	−21.8127	−22.4445	−23.0710	−23.6925
1800	−19.9600	−20.6070	−21.2485	−21.8847	−22.5156	−23.1414	−23.7620
1850	−20.0523	−20.6977	−21.3377	−21.9723	−22.6016	−23.2258	−23.8450
1900	−20.1622	−20.8052	−21.4427	−22.0750	−22.7019	−23.3238	−23.9405
1950	−20.2893	−20.9290	−21.5633	−22.1922	−22.8158	−23.4343	−24.0477
2000	−20.4333	−21.0687	−21.6986	−22.3232	−22.9425	−23.5567	−24.1657
2050	−20.5936	−21.2235	−21.8480	−22.4672	−23.0811	−23.6898	−24.2935
2100	−20.7697	−21.3930	−22.0109	−22.6234	−23.2307	−23.8328	−24.4299
2150	−20.9609	−21.5763	−22.1863	−22.7909	−23.3903	−23.9845	−24.5736
2200	−21.1665	−21.7726	−22.3733	−22.9686	−23.5587	−24.1436	−24.7235

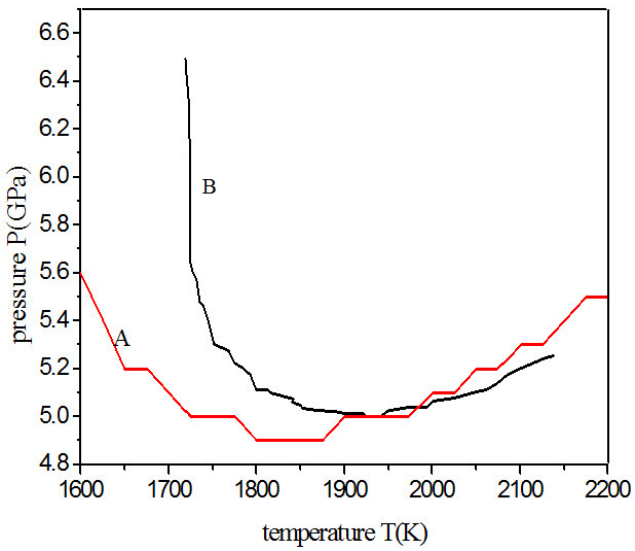
We show the results in Table 4 supposing that Li_3BN_2 could decompose into cBN. We find that when the pressure is as low as 4.8 GPa, ΔG is negative and ΔG increases from negative to positive with increasing temperature and pressure. ΔG increases from negative to positive with increasing pressure when the temperature is constant. However, ΔG increases first and then decreases with the increasing temperature under constant pressure, and ΔG of reaction Li_3BN_2→cBN + Li_3N can be negative or positive when the pressure is between 4.8 and 6.0 GPa. It can be obtained from Table 4 that the boundary of negative and positive values forms an approximate V-shaped area (the upper area of curve A in Figure 1), in which ΔG of reaction Li_3BN_2→cBN + Li_3N is positive and this reaction does not occur. Therefore Li_3BN_2 can exist stably, and cBN does not come from the decomposition of Li_3BN_2 in the V-shaped area. Upper area of Curve B in Figure 1 is the V-shaped area from [8] where cBN can grow stably. Figure 1 indicates that the V-shaped area formed in Table 4 covers the most part of the V-shaped area of cBN growth from the references. In other words, the reaction Li_3BN_2→cBN + Li_3N cannot occur in the V-shaped area where the macroaggregated and high-quality cBN crystals can be obtained. That is to say, cBN cannot be produced by the treatment of only Li_3BN_2 in the V-shaped area

obtained from Table 4. However, it can be seen from Table 3 that in the same area, ΔG of the hBN-cBN transition is negative, and it becomes more and more negative with increasing temperature and pressure. We speculate that in the V-shaped area, cBN is probably transformed directly from hBN.

Table 4. ΔG of $Li_3BN_2 \rightarrow cBN + Li_3N$ at different temperatures and pressures.

T/K	ΔG/(KJ·mol^{-1})						
	4.8 GPa	**5.0 GPa**	**5.2 GPa**	**5.4 GPa**	**5.6 GPa**	**5.8 GPa**	**6.0 GPa**
1600	−3.3405	−2.4757	−1.6792	−0.8553	−0.0358	0.7795	1.5904
1650	−2.4247	−1.4193	−0.4822	0.4824	1.4426	2.3984	3.3500
1700	−1.7134	−0.5583	0.5285	1.6427	2.7525	3.8580	4.9592
1750	−1.2296	0.0842	1.3297	2.6026	3.8712	5.1354	6.3953
1800	−0.9970	0.4846	1.8979	3.3386	4.7750	6.2070	7.6347
1850	−1.0401	0.5865	2.2086	3.8263	5.4395	7.0484	8.6530
1900	−1.3837	0.4289	2.2370	4.0406	5.8399	7.6348	9.4254
1950	−2.0537	−0.0459	1.9573	3.9561	5.9505	7.9405	9.9263
2000	−3.0760	−0.8640	1.3434	3.5464	5.7451	7.9393	10.1293
2050	−4.4774	−2.0521	0.3686	2.7849	5.1968	7.6043	10.0076
2100	−6.2851	−3.6376	−0.9945	1.6440	4.2783	6.9081	9.5337
2150	−8.5270	−5.6482	−2.7739	0.0960	2.9615	5.8226	8.6795
2200	−11.2312	−8.1122	−4.9977	−1.8877	1.2180	4.3193	7.4164

Figure 1. The V-shaped area of $\Delta G > 0$ of Li_3BN_2 decomposition and V-shaped area of cBN growth. (A) The V-shaped area of $\Delta G > 0$ of Li_3BN_2 decomposition. (B) The V-shaped area of cBN growth [3].



It is known from [2] that cBN does not form when Li_3BN_2 melts or decomposes, and only when excess hBN is added can cBN be found. Li_3BN_2 exists stably in the HPHT area of cBN growth, and Li_3BN_2 appears to be in equilibrium with cBN in the Li_3N-hBN system. We infer that the catalyst promotes the transition of hBN to cBN. The melting point of hBN is over 3000 K at ambient pressure. hBN has a stable structure with a sp^2 hybridization state in the hexagonal ring layer and Van der Waals' force between layers. The hybridized orbital of B atom is $sp^2 + 2p^0$, and N atom is $2s^2 + 2p^2$ in hBN.

However, the hybridized orbital of B and N atom is sp^3 in cBN, and the chemical bond between B and N atom is a stable σ-bond, so the most important driving force for the transition from hBN to cBN is to transfer an electron from N atom to B atom. Part of Li^+ in the short-range ordered structure of Li_3BN_2 absorbs electrons from N atom at the high active state. Because of its instability, Li cannot exist stably in the high temperature and high pressure system. B atoms with empty orbitals absorb the electrons of Li, and then complete the electronic transfer from N to B atoms [21], so both the electrical structures of the B and N atoms are $sp^2 + 2p^1$. Electrons in the s orbital of B and N atoms at the high temperature are excited into the empty p orbitals. The B and N atom can form a sp^3 hybridization state. B and N atoms in this sp^3 hybridization state form σ covalent bonds in a head-to-head mode with energy fluctuations, and generate the microstructure of cBN at high pressure and high temperature.

Li_3BN_2 is short-range ordered at molten-like state under HTHP, and it can be dissolved into well-ordered hBN. BN_2^{3-} ion invades hBN and affects the van der Waals forces between the layers, causing inter-layer slippage or breakage. hBN can be disintegrated into two dimensional B-N dusts with low polymerization degree. At this time, the long-range ordered structure disappears, rendering a short-range ordered structure. Without catalyst, higher temperatures than 3000 K and higher pressures than 13 GPa are needed to obtain cBN crystals [4]. With the catalyst, a short-range or medium-range ordered molten-like structure [5] forms to greatly reduce the temperature and pressure of cBN synthesis. From the point of crystal nucleation, the B-N dusts produced by hBN degradation can transform into cBN microstructures by heterogeneous nucleation with energy fluctuation [22]. Li_3BN_2 could be the matrix of cBN nucleation, because of the similar crystal structure and larger lattice constant [23]. The process only forms the microstructure of cBN crystals. In order to obtain cBN crystals, it is essential for the tiny crystal nucleus to grow gradually [24].

4. Conclusions

(1) In the HPHT area (1600~2200 K, 4.8~6.0 GPa) of cBN growth, the reaction $hBN + Li_3N \rightarrow Li_3BN_2$ can occur, and the ΔG of the reaction is between −35 and −10 $KJ \cdot mol^{-1}$. However, in the same P-T area, ΔG of transition hBN→cBN is between −25 and −19 $KJ \cdot mol^{-1}$, indicating a more probable transition. The ΔG of decomposition $Li_3BN_2 \rightarrow cBN + Li_3N$ is almost positive, thus Li_3BN_2 can exist stably.

(2) The area of the positive ΔG of Li_3BN_2 decomposition forms an approximate V-shaped area, which covers the most part of the V-shaped area of cBN crystal growth. Therefore, cBN does not come from the decomposition of Li_3BN_2 and cBN is probably transformed from hBN. However, analysis shows that Li_3BN_2 promotes the transfer of an electron from a N atom to a B atom in order to form the micro cBN nuclei.

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Author Contributions

Bin Xu made substantial contributions to conception and design of this paper. Bin Xu, Mei-Zhe Lv and Hong-Mei Yang performed acquisition, analysis, and interpretation of data. Mei-Zhe Lv and Hong-Mei Yang drafted the paper; Zhen-Xing Wen participated in analysis and interpretation of data, and gave useful suggestions for revising the manuscript; Bin Xu gave final approval of the version to be submitted and any revised version. All authors read and approved the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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