Письма в редакцию

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Phase diagram of the B–B_2O_3 system at pressures to 24 GPa

The evolution of topology of the B–B_2O_3 phase diagram has been studied at pressures up to 24 GPa using models of phenomenological thermodynamics with interaction parameters derived from experimental data on phase equilibria at high pressures and high temperatures.

***Keywords**: B–B_2O_3 system, high pressure, high temperature, phase diagram.*

The B–B_2O_3 system that includes superhard refractory boron suboxide, B_6O [1] (and possibly some novel superhard high-pressure phases [2, 3]) has been previously studied at pressure of 5 GPa [4]. However, very recently Solozhenko et al. have revised the *p-T* phase diagram of boron oxide, B_2O_3 and refined the location of the α-B_2O_3–β-B_2O_3–L triple point as 5.4 GPa / 1550 K [5]. This means that at 5 GPa the melting of α-B_2O_3 takes place, and not of β-B_2O_3, as previously thought [4, 6]. Also the new equilibrium *p-T* phase diagram of boron [7] should be taken into account. In the present study we performed thermodynamic calculations of high-pressure phase equilibria in the B–B_2O_3 system using the revised data and constructed phase diagrams at different pressures.

The calculations were carried out using the Thermo-Calc software [8]. Thermodynamic data of phases of the B–B_2O_3 system at ambient pressure were taken from [4]. The liquid phase was described using the subregular solution model [9], and solid phases – in the framework of the Compound Energy Formalism (CEF) [10]. Pressure dependencies of molar volumes were represented using the Murnaghan approximation [11]. Bulk moduli, their pressure derivatives, and thermal expansion coefficients for B_6O and B_2O_3 were taken from [1, 5], and the data on liquid phase, β-B_{106}, γ-B_{28}, and t′-B_{52}, – from [7, 12, 13]. Parameters of the pressure dependencies of the Gibbs energy of the phases in the B–B_2O_3 system are listed in the table.

Parameters of the pressure dependencies of the Gibbs energy

Phase	V_0, m^3/mol	B, GPa	B′	α_0	α_1
α-B_2O_3	$27.25\cdot10^{-6}$	40	5.5	$3.0\cdot10^{-5}$	$1.6\cdot10^{-7}$
β–B_2O_3	$22.38\cdot10^{-6}$	170	5.0	$1.5\cdot10^{-5}$	$2.32\cdot10^{-8}$
B_6O	$31.5\cdot10^{-6}$	180	6.0	$1.5\cdot10^{-5}$	$1.12\cdot10^{-8}$
β-B_{106}	$4.737\cdot10^{-6}$	210	2.23	$1.57\cdot10^{-6}$	$2.64\cdot10^{-8}$
γ-B_{28}	$4.347\cdot10^{-6}$	237	2.7	$1.57\cdot10^{-6}$	$2.64\cdot10^{-8}$
t′-B_{52}	$4.362\cdot10^{-6}$	237	2.7	$1.57\cdot10^{-6}$	$2.64\cdot10^{-8}$

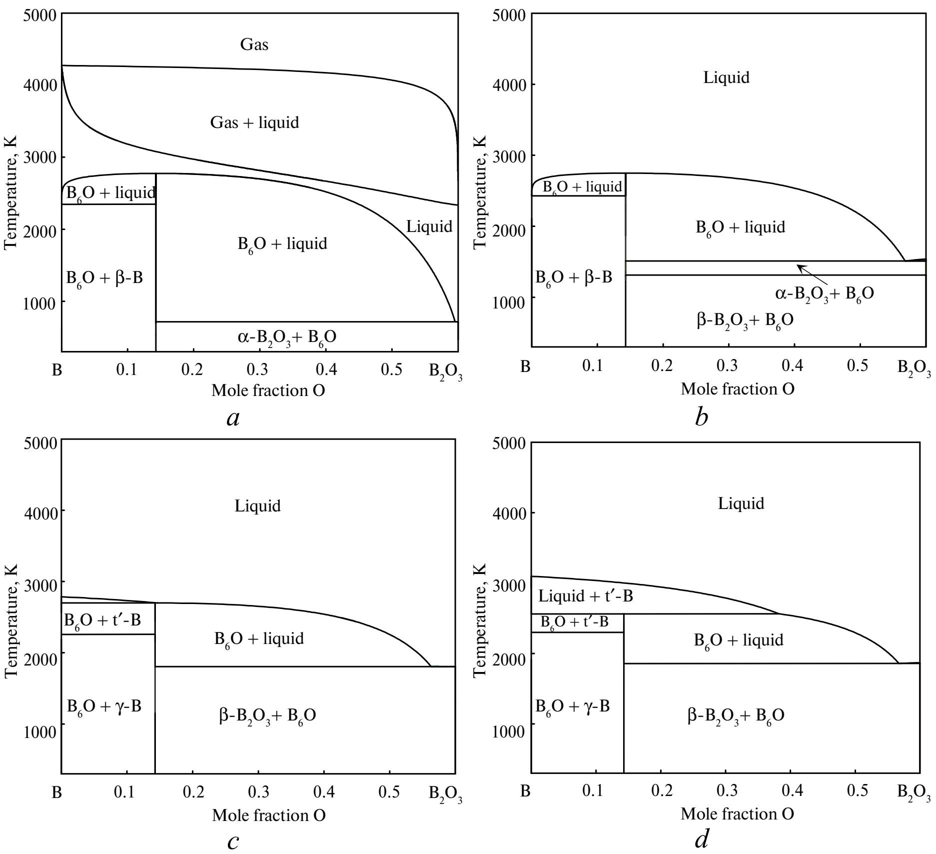
V_0 is the molar volume; B is the bulk modulus; B′ = dB/dp; $\alpha = \alpha_0 + \alpha_1 T$ is the volume thermal expansion coefficient.

The molar volume of the liquid phase was described by the equation:

$$V_L = V_B x_B + V_{B_2O_3} x_{B_2O_3}\ .$$

Gas phase was considered as ideal gas.

The evolution of the phase diagram of the B–B_2O_3 system under pressure is shown in the figure. In addition to the quantitative changes of the diagram parameters (equilibria temperatures, limiting solubilities), changes of the diagram topology are observed i.e., above 8.5 GPa the γ-B_{28} ⇄ t′-B_{52} equilibrium line appears; the congruent type of B_6O melting changes to the incongruent one at about 16 GPa, and the L ⇄ β-B_{106} + B_6O eutectic changes to the L + t′-B_{52} ⇄ B_6O peritectic.



Phase diagram of the B–B_2O_3 system at 0.1 MPa (*a*), 5 GPa (*b*), 16 GPa (*c*) and 24 GPa (*d*); β, γ, t′ are boron allotropes (β-B_{106}, γ-B_{28} and t′-B_{52}, respectively).

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Вивчено еволюцію топології фазового діаграми $B–B_2O_3$ при тисках до 24 ГПа з використанням моделей феноменологічної термодинаміки з параметрами взаємодії, отриманими з експериментальних даних про фазову рівновагу при високих тисках і високих температурах.

***Ключові слова**: система $B–B_2O_3$, високий тиск, висока температура, фазова діаграма.*

Изучена эволюция топологии фазового диаграммы $B–B_2O_3$ при давлениях до 24 ГПа с использованием моделей феноменологической термодинамики с параметрами взаимодействия, полученными из экспериментальных данных о фазовом равновесии при высоких давлениях и высоких температурах.

***Ключевые слова**: система $B–B_2O_3$, высокое давление, высокая температура, фазовая диаграмма.*

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