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Equations of state of novel solids synthesized under extreme pressure–temperature conditions

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Abstract. The pressure-volume-temperature equations of state have been constructed by combining experimental data and semiempirical estimations for a number of compounds recently synthesized under extreme pressure-temperature conditions. The solids with various bonding types were considered: covalent hard and superhard boron-rich and diamond-like compounds (e.g. B_6O, $B_{13}N_2$, BP, c-BC_5, and nano-cBN), ionic semiconductors (e.g. Mg_2C and Mg_2C_3), as well as intercalation compounds (e.g. clathrates Na_4Si_{24} and $Na_{24+x}Si_{136}$), and simple substances (e.g. boron allotropes γ-B_{28} and t′-B_{52}, and open-framework silicon allotrope o-Si_{24} with quasi-direct bandgap). We also showed how the reliable p-V-T equations of state may be constructed using different types of data available.

1. Introduction

Recently high pressure–high temperature (HPHT) large-volume synthesis allowed obtaining a number of novel materials [1] for new challenging applications as superhard [2–6], advanced electronic [7], photovoltaic [8] and thermoelectric [9, 10] materials, as well as superconductors [11, 12]: (i) boron allotropes [13, 14] (orthorhombic γ-B_{28} [15–17], pseudo-cubic t′-B_{52} [18]) and boron-rich compounds (boron subnitride $B_{13}N_2$ [19, 20]), (ii) superhard compounds with diamond structure (nanostructured cBN [21], non-stoichiometric c-BC_5 [22, 23]); (iii) covalent clathrates of new stoichiometries ($Na_{4-x}Si_{24}$ [8, 9] and $Na_{24+x}Si_{136}$ [9, 10]) and even (iv) new unexpected semiconductors, like antifluorite Mg_2C [24], dense Mg_2C_3 [25] and pure silicon allotrope with quasi-direct bandgap, Si_{24} [8].

For understanding of phase transformations and chemical interactions in the corresponding systems, one needs to explore the thermodynamics under HPHT conditions. And, although a part of the lacking data can be replaced by fitted parameters of common models [26–28] or with *ab initio* calculations [29], the reliable p-V-T equations of state (EOS) data are crucial for that. In the present paper we describe the method of construction of such equations of state using integrated form of the Anderson-Grüneisen equation [30, 31]. The method is efficient even in the case of small number of experimental data [32] and may be easily combined with *ab initio*, semiempirical and even empirical modeling.

2. Theoretical background

In our previous works [32, 33] we have shown that the Anderson-Grüneisen equation [30, 31], which takes into account the pressure dependence of thermal expansion through the volume change, i.e.

$$\alpha(p,T) = \alpha(0,T)\left[\frac{V(p,T)}{V(0,T)}\right]^{\delta_T}, \tag{1}$$

can be integrated (under the assumption that δ_T is constant) to

$$V(p,T) = \Big[V(0,T)^{-\delta_T} + V(p,300)^{-\delta_T} - V(0,300)^{-\delta_T}\Big]^{-1/\delta_T}, \tag{2}$$

where thermal expansion (i.e. $V(0,T)$ at 0.1 MPa) and isothermal compression (i.e. $V(p{,}300)$ at 300 K) can be presented in any analytical form, e.g. polynomial

$$V(0,T) = V_0(1 + a(T-300) + b(T-300)^2), \tag{3}$$

and Vinet equation of state [34]

$$p(V,300) = 3B_0\,(V/V_0)^{-2/3}\left[1-(V/V_0)^{1/3}\right]e^{1.5(B_0'-1)\left[1-(V/V_0)^{1/3}\right]}. \tag{4}$$

Finally, the set of parameters needed to describe an EOS in the form (2) is $V_0 = V(0{,}300) = M/\rho_0$, B_0, B_0', a, b and δ_T (usually between 4 and 6). And the Gibbs potential can be calculated as

$$\begin{aligned}G(p,T) &= G(0,T) + \int_0^p V(\pi,T)d\pi\\ &= G(0,T) + \int_0^p \Big[V(0,T)^{-\delta_T} + V(\pi,300)^{-\delta_T} - V(0,300)^{-\delta_T}\Big]^{-1/\delta_T} d\pi.\end{aligned} \tag{5}$$

Such form of the EOS (2) allows one easily approximate the $V(p,T)$ in the vicinity of a new compound formation, which is often the principal domain of interest in the terms of HPHT thermodynamics. Here the unit cell volume can be estimated *in situ* using x-ray diffraction (300-K EOS may be measured on decompression).

In some other cases, the knowledge of phase equilibrium curves may allow evaluating the HPHT EOS of unknown phase through the known one. For example, we succeeded to fit the experimental melting curves (p-T coordinates) of α- and β-B_2O_3 and to find the parameters determining the p-V-T EOS for liquid B_2O_3 (the results will be published elsewhere). The melting was observed experimentally, while the bulk modulus and thermal expansion parameters were adjusted so that the experimental curve fits the theoretical one.

3. EOS data and discussion

Table 1 shows the p-V-T EOS data available from the experiment or estimated using various models (marked with an asterix in the table) for boron and boron-rich, diamond-like, Mg-C and Na-Si compounds.

In the case of boron-rich solids the only unknown bulk modulus, that of pseudo-cubic t′-B_{52} phase was estimated using the density data by the method described elsewhere for various elastic characteristics of covalent and ionic materials [35–38] and previously justified for boron allotropes [39]. At the same time, the thermal expansion parameters are known just for B_6O [40, 41]. For both dense allotropes, γ-B_{28} and t′-B_{52}, we propose to take, in the first approximation, values of β-B_{106} [42], while for boron subnitride $B_{13}N_2$ one can take a value

Table 1. p-V-T equation of state data for compounds synthesized at high pressure. Units: ρ in g/cm^3; B_0 in GPa; B_0' is dimensionless; a in 10^6 K^{-1}; b in 10^9 K^{-2}; δ_T is dimensionless.

	Phase	Parameters of EOS
Boron-rich solids	γ-B_{28}	$\rho_0 = 2.544$, $B_0 = 237$, $B_0' = 2.7$,
	[39,43]	$a = 18^*$, $b = 0^*$ and $\delta_T = 5.5^*$
	t′-B_{52}	$\rho_0 = 2.493$, $B_0 = 232^*$, $B_0' = 2.7^*$,
	[18]	$a = 18^*$, $b = 0^*$ and $\delta_T = 5.5^*$
	B_6O	$\rho_0 = 2.601$, $B_0 = 180$, $B_0' = 6$,
	[32,33,44]	$a = 14^*$, $b = 5^*$ and $\delta_T = 6$
	$B_{13}N_2$	$\rho_0 = 2.666$, $B_0 = 200$, $B_0' = 4.0$,
	[26,45]	$a = 14^*$, $b = 5^*$ and $\delta_T = 5.5^*$
Diamond-like phases	Nano-cBN	$\rho_0 = 3.615$, $B_0 = 375$, $B_0' = 2.3$,
	[46,47]	$a = 15^*$, $b = 0^*$ and $\delta_T = 5.5^*$
	c-BC_5	$\rho_0 = 3.267$, $B_0 = 335$, $B_0' = 4.5$,
	[22]	$a = 13^*$, $b = 0^*$ and $\delta_T = 5.5^*$
	BP	$\rho_0 = 2.966$, $B_0 = 174$, $B_0' = 3.2$,
	[48–50]	$a = 16.5$, $b = 0$ and $\delta_T = 5.5^*$
Mg-C system	Mg_2C	$\rho_0 = 2.503$, $B_0 = 87$, $B_0' = 5.1$,
	[24,29]	$a = 48$, $b = 7.1$ and $\delta_T = 4.3$
	β-Mg_2C_3	$\rho_0 = 2.580$, $B_0 = 103$, $B_0' = 4.0$,
	[25]	$a = 48^*$, $b = 7.1^*$ and $\delta_T = 5.5^*$
Na-Si system	$Na_{24+x}Si_{136}$	$\rho_0 = 2.318$, $B_0 = 90^*$, $B_0' = 4^*$,
	[10]	$a = 17$, $b = 0$ and $\delta_T = 5.5^*$
	Na_4Si_{24}	$\rho_0 = 2.395$, $B_0 = 90^*$, $B_0' = 4^*$,
	[9]	$a = 17^*$, $b = 0^*$ and $\delta_T = 5.5^*$
	Si_{24}	$\rho_0 = 2.163$, $B_0 = 90^*$, $B_0' = 4^*$,
	[8]	$a = 12^*$, $b = 0^*$ and $\delta_T = 5.5^*$

of suboxide B_6O having similar crystal structure. Except for B_6O, the δ_T parameter—linking 300-K p-V data with 0.1-MPa thermal expansion data—was fixed to 5.5. Figure 1 shows that the parameters well agree with experimental *in situ* observations for $B_{13}N_2$. Better fit may be obtained with $\delta_T = B_0' = 4$ (just like in the case of B_6O, $\delta_T = B_0' = 6$) or by adjusting the a and b thermal expansion parameters, or even by suggestion of a pressure drop from 5 to 4 GPa. So, the lack of experimental data does not allow making a choice, and so far we suggest a value of $\delta_T = 5.5$.

For diamond-like phases (nano-cBN, c-BC_5 and BP), as well as for Mg-C compounds, all bulk moduli were established experimentally. Only for BP the thermal expansion data at 0.1 MPa have been available in literature. In the case of Mg_2C the a and b parameters were established by fitting the p-V data at high temperature (around 1500 K) [29], while in other cases they were estimated from the literature data (for nano-cBN—its conventional counterpart [46], for c-BC_5—the linear combination of diamond [51] and boron [42]). $\delta_T$parameter was chosen as 5.5 for all compounds except Mg_2C. Figure 2 shows that the parameters well agree with experimental *in situ* observations for c-BC_5. Just like in the case of $B_{13}N_2$ discussed above, the "ideal" match of an experimental point to the theoretical curve may be achieved, but it is not clear which parameter should be used for such adjustment (e.g. a or pressure drop during the

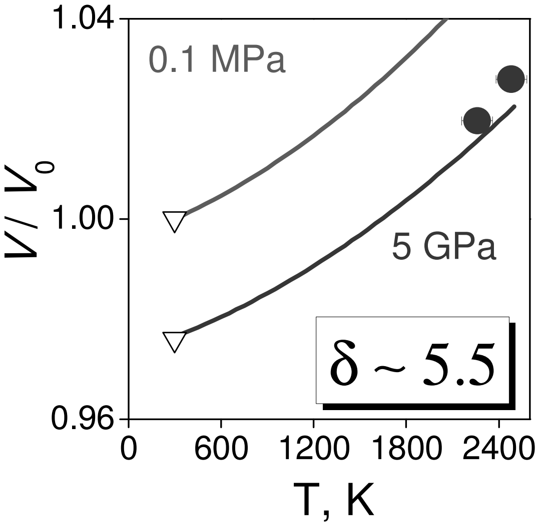

Figure 1. p-V-T equation of state of $B_{13}N_2$. Experimental points obtained at HASYLAB (multianvil press MAX80, resistive heating).

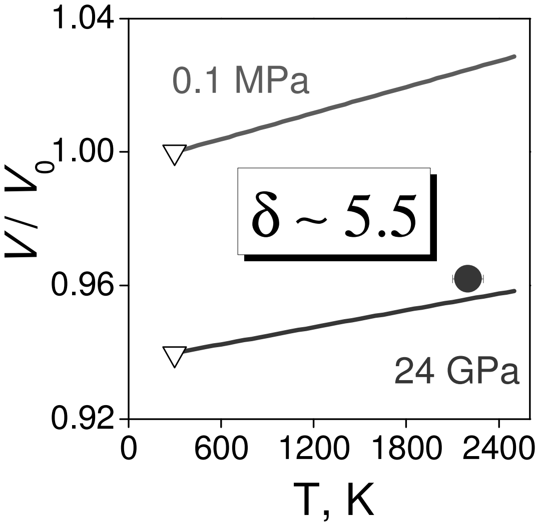

Figure 2. p-V-T equation of state of c-BC_5. Experimental points obtained at ESRF (diamond anvil cell, laser heating).

transformation).

In the case of clathrate compounds of the Na-Si system the situation with the data is the most complicated. High-temperature data, especially, at low pressure can hardly be obtained, since the compounds easily decompose. From another side, at high pressure these compounds often have only narrow domains of stability. However, it has been established that elastic properties mainly depend on the rigid silicon framework and are close to those of diamond silicon [52, 53].

For $Na_{24+x}Si_{136}$ and Na_4Si_{24} the values of bulk moduli were fixed to that of $Na_{24}Si_{136}$, while for open framework “high-pressure” clathrate silicon, to the values of Si_{136} [53,54]. The experimental results on these compounds will be published elsewhere.

4. Conclusion

Finally, we have proposed a set of parameters that allow one to construct p-V-T equations of state for a number of newly discovered high-pressure solids. The reported data give a first approximation of the parameters for the construction of high-pressure phase diagrams with participation of boron for new advanced materials, as well as for the Mg-C and Na-Si systems, promising for production of unique semiconductive diamonds [55] and advanced silicon for optoelectronic applications [8].

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