NEW METHODS TO GROW DIAMOND AND CUBIC BORON NITRIDE

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On Earth (now) *significantly more* natural graphite (G) than diamond (D) is mined/processed, and *significantly more* synthetic G than D is made. In metric tons: Natural G(1,500,000) vs D(24) and Synthetic G(3,500,000) vs D (3,100).

D&G are almost isoenergetic at 273K and 1 atm and the same is true for hexagonal boron nitride (hBN) and cubic boron nitride (cBN). A pure carbon sample containing only D&G at chemical equilibrium would have ~22 mol% D at STP and about 34.5 mol% at 2000K (per HSC Chemistry). ΔH_f of D at STP is about the same as ΔH_{vap} of liquid neon at its bp of 27K, and about 1/10 the H-bond enthalpy in liquid water. (We recall that graphite is the standard state at STP.)

My perspective: I will explain that **kinetic control** and *not* thermodynamic control dictates why it has been simpler to synthesize G than D at <u>1 atm pressure</u>. And rather interestingly (if I am correct—and I welcome discussion) in high temperature-<u>high pressure</u> (HTHP) synthesis of D in metal flux it is also **kinetic control** and *not* thermodynamic control that favors synthesis of D vs G (pressures in the range 5 – 10 GPa). Almost invariably the explanation for each case (e.g., in textbooks, the published literature, etc.) has been based on thermodynamics and I find this "simply wrong" in both cases.

I discuss possibilities to synthesize D (please see [1]) in *new ways*. The parameter space for the elemental compositions of metal fluxes that might dissolve the needed amount of C (or for cBN the needed amount(s) of B and/or N) at ~1 atm pressure is *very large* as readily obtained from combinatorics and the relevant elements in the Periodic Table. Fortunately (for basic science as well as possibilities for new technologies) there is a great deal that is "not studied at all" about phase equilibria and dissolution of carbon in many possible metal flux choices.

I look forward to presenting new ideas about establishing/controlling the spatiotemporal distribution of solute elements in metal flux, from "time = 0" onwards (as the metal flux system evolves, so to speak). With **retrosynthesis** (...**inverse design**, **inverse optimization**) and **kinetic control** rather deeply on my mind, I foresee a new—and very promising— horizon for synthesis of diamond and cubic boron nitride. *Supported by the Institute for Basic Science (IBS-R019D1)*.

References

[1] Yan Gong, Da Luo, Myeonggi Choe, Won Kyung Seong, Pavel Bakharev, Meihui Wang, Seulyi Lee, Tae Joo Shin Zonghoon Lee, Rodney Ruoff. Growth of diamond in liquid metal at 1 atmosphere pressure. *Nature*. 2023, 629, 348-354.