

Direct diamondoid-to-diamond phase transitions

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Pressure-temperature-phase space of carbon-hydrogen systems has been a topic of intense investigation due to their importance in a wide range of fields, ranging from planetary sciences to condensed matter physics. Here, we explore how diamondoids, a unique class of hydrogen-terminated carbon nanomaterials, undergo phase and chemical transformations, and dissociate into various carbon forms under static compression and high temperature. Entirely constituted by sp^3 bonded carbon atoms superimposed on the cubic diamond lattice and terminated by hydrogen atoms, diamondoid molecules are stiff, dense, and contain exceptional properties of both bulk diamond and small hydrocarbon molecules [1]. This makes diamondoids attractive for a wide range of applications, ranging from polymer synthesis, nanotechnology, drug delivery, drug targeting to molecular electronics.

At high pressure and ambient temperature, bulk moduli of diamondoid crystals are dependent on their molecular geometry, wherein a higher dimensionality of a diamondoid molecule (as opposed to the simple packing schemes within the unit cell) yields a lower compressibility [2]. At high pressure and high temperature, all diamondoids studied exhibit direct diamondoid-to-graphite and diamondoid-to-diamond phase transitions. The pressure and temperature needed for the diamondoid-to-diamond conversion is significantly lower than those for graphite [3] and other hydrocarbons (e.g., polycyclic aromatic hydrocarbons [4]). For instance, triamantane transforms into diamond at 15 GPa with a temperature onset of 1200 K. In comparison, graphite was reported to transform to diamond at > 2000 K at 15 GPa [3]. The significantly lowered temperature onset suggests that diamondoids are optimal seed materials for diamond synthesis. Similar to the influence on their bulk moduli, the nature of the initial dimensionality and the C-H ratio of diamondoids influence the diamond stability field.

[1] J. E. Dahl, S. G. Liu, and R. M. K. Carlson. "Isolation and structure of higher diamondoids, nanometer-sized diamond molecules". *Science* 2003, 299, 96

[2] F. Yang, Y. Lin, J. E. P. Dahl, R. M. K. Carlson, and W. L. Mao. "Effects of molecular geometry on the properties of compressed diamondoid crystals". *J. Phys. Chem. Lett.* 2016, 7, 4641

[3] T. Irifune, A. Kurio, S. Sakamoto, T. Inoue, H. Sumiya, and K. I. Funakoshi. "Formation of pure polycrystalline diamond by direct conversion of graphite at high pressure and high temperature" *Physics of the earth and planet interiors. Phys. Earth Planet. Inter.* 2004, 143-144, 593

[4] Davydov, V. A. *et al.* "Conversion of polycyclic aromatic hydrocarbons to graphite and diamond at high pressures". *Carbon, Elsevier*, 2005, 42, 261