

Kinetic Origin of Phase Transformation Pathways in Carbon, Silicon and Germanium

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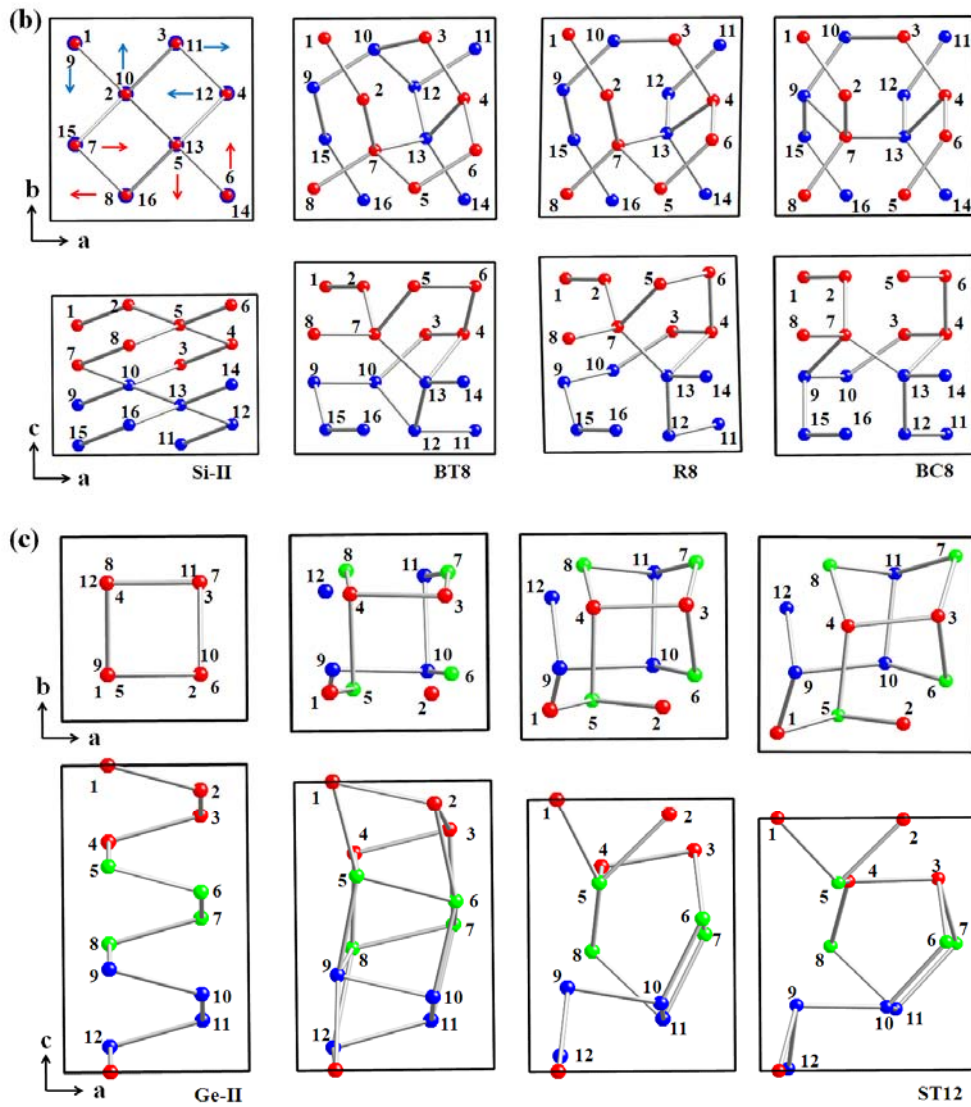
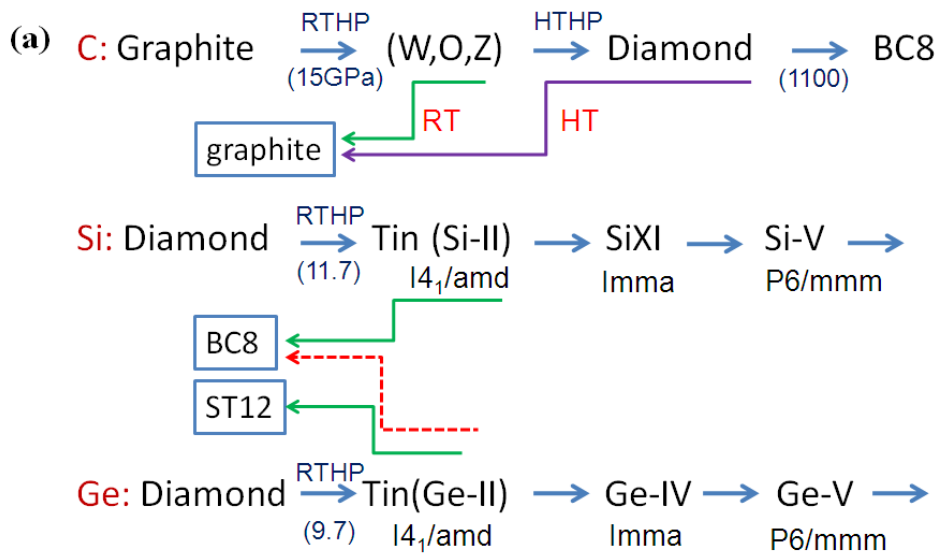
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At ambient conditions carbon exists in the form of graphite that transforms at room temperature to diamond-like structures (W, Z, O, J carbon) at pressures above 15 GPa. These structural transformations are reversible, and upon decompression graphite is recovered [1]. More intriguing, however, are the phase transitions of silicon and germanium that crystallize at ambient conditions in the cubic diamond structure (Si-I or Ge-I) and transform to a body-centered tetragonal β -tin structure (Si-II or Ge-II) at 11.7 GPa and 9.7 GPa, respectively. Upon slow decompression, instead of returning to the most stable diamond structure, divergent transformation pathways lead to a body-centered cubic structure (BC8) for silicon or a simple tetragonal structure (ST12) for germanium [see Fig. (a)]. In this work, we report on a first-principles study of energetics and kinetics for the phase transition upon decompression in Si and Ge from the β -tin phase. We have identified two basic reconstruction pathways, one toward the BC8 Si via a double cell in-plane local-bond-rotation reconstruction mechanism [see Fig. (b)], and the other toward the ST12 Ge via a trinary cell local-bond-twisting reconstruction mechanism [see Fig. (c)]. The pathways to return to the most stable diamond structure are inhibited by the higher kinetic barriers in both cases. Moreover, a metastable tetragonal BT8 structure in $I4_1/a$ symmetry has been identified as an intermediate structure between the Si-II and BC8 Si phase that facilitates the structural reconstruction. This new phase as a precursory state of the BC8 phase is also viable in Ge under special conditions such as a rapid pressure release; but the primary decompressed ST12 Ge phase dominates when the pressure release is slow and the system has sufficient time to follow the energetically most favorable pathway that is also kinetically competitive. The crucial role of kinetics in selecting the divergent decompression pathways explains the intriguing structural transformations observed in Si and Ge [2].



[1] J. T. Wang, C. F. Chen, and Y. Kawazoe, Phys. Rev. Lett. **106**, 075501 (2011); Phys. Rev. B. **84**, 012102 (2011); Phys. Rev. B. **85**, 033410 (2012); J. Chem. Phys. **137**, 024502 (2012).

[2] J. T. Wang, C. F. Chen, H. Mizuseki, and Y. Kawazoe, Phys. Rev. Lett. **110**, 165503 (2013).