

Mechanisms of silicon and carbon allotropes' crystallization in condensed media by in situ diffraction of synchrotron radiation

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Silicon. HP research on Si started more than 50 years ago and since then several allotropes, displaying a wide variety of physical properties, have been reported.¹⁻⁵

The narrow-bandgap semiconductor⁶ Si-III⁴ with BC8 structure (originally believed to be semimetal) can be obtained from the high-pressure tetragonal metallic phase, Si-II, formed during compression of common silicon according to Si-I→Si-III. Such a transformation during decompression can be either direct, Si-II→Si-III, or with an intermediate step Si-II→Si-XII→Si-III. Our in situ studies of pure Si in oxygen-free environment indicated that in the absence of pressure medium, Si-I remains metastable at least up to ~14 GPa, while the pressure medium allows reducing the onset pressure of transformation to ~10 GPa.

Upon heating Si-III at ambient pressure a hexagonal structure, named Si-IV, was observed. This allotrope was believed to be a structural analogue of the hexagonal diamond found in meteorites (called also lonsdaleite) with the 2H polytype structure. Calculations have predicted several hexagonal polytypes of Si and of other Group-IV elements to be metastable, such as 2H (AB), 4H (ABCB) and 6H (ABCACB). Exhaustive structural analysis, combining fine-powder X-ray and electron diffraction, afforded resolution of the crystal structure. We demonstrate that hexagonal Si obtained by high-pressure synthesis correspond to Si-4H polytype (ABCB stacking),⁵ in contrast with Si-2H (AB stacking) proposed previously. The sequence of transformations Si-III→Si-IV(4H)→Si-IV(6H) has been observed in situ by powder X-ray diffraction. This result agrees with prior calculations that predicted a higher stability of the 4H form over 2H form. Further physical characterization, combining experimental data and ab-initio calculations, have shown a good agreement with the established structure. Strong photoluminescence emission was observed in the visible region, for which we foresee optimistic perspectives for the use of this material in Si-based photovoltaics.

The study of silicon allotropic transformation in Na-Si and K-Si systems at high pressure, high temperature conditions indicated new interesting results on the second-order character of Si-II→Si-XI transformation and will be discussed in the presentation. The impact of the second order character on the topology of the pressure-temperature phase diagram of silicon will be analyzed.

Carbon. The most common polytypes of carbon in graphitic (G) form are hexagonal (2H) and rhombohedral (3R) polytypes, which allow quasi-martensitic transformation into diamond (D) forms, such as hexagonal diamond 2H or common cubic diamond 3C, at HP and moderate temperatures (~1000 – 1500 K), e.g. G-2H→D-2H or G-3R→D-3C. High temperatures lead to the formation of thermodynamically stable allotropes, G-3R→G-2H at ambient pressure and D-2H→D-3C at high pressures.

Graphite intercalation compounds (GIC) with metals such as Li, Na and K form different compositions (and crystal structures) produced by stacking along c-axis of metal (Me) and *n* carbon (A, B or C) layers. The *n* number indicate the stage of intercalation. Typically ordered compounds are obtained for *n* = 1 to 6 with various stacking sequences depending on metals: *n* = 1 for MeAMeB, *n* = 2 for MeABMeBAMeCA, *n* = 3 for MeABCMeBCAMeCAB, etc. High pressure studies has been performed principally on 1st stage compounds of Li and K, while formation of 1st stage Na-C compound has been observed only at HPHT conditions. In this presentation we will discuss the structural features of GIC, the XRD, Raman and other structurally related data, as well as corresponding “diamond intercalation compounds” (DIC) structurally related to GIC and their possibility to form at HPHT conditions.

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