

Phase diagram of carbon dioxide revisited

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Carbon dioxide, CO₂, is one of the most important compounds in nature and the second most abundant volatile in the Earth's interior. Its structure and properties at high pressures and temperatures pertaining to geoscience are crucial both to fundamental chemistry and solid state physics.

CO₂ has a very complex phase diagram consisting of a number of crystalline molecular phases below 40 GPa. On further compression it polymerizes forming at moderate temperatures (up to 680 K) amorphous glass with carbon in threefold and fourfold coordination [1], while the laser heating above 1800 K/40 GPa produces a polymeric covalent crystal phase (CO₂-V, space group *I*4̄2*d*) that can be described as a network of fourfold coordinated carbon atoms interconnected by oxygen bridges resembling structurally β-cristobalite (SiO₂) [2].

The substantial kinetic barrier, reflecting dramatic changes in the bonding scheme on transition to the polymeric phase, led to numerous observations of metastable states in the stability field of CO₂-V, causing controversies. Hence, we have decided to investigate the chemical and phase stability of carbon dioxide at pressures up to 120 GPa [3] and temperatures reaching 6000 K [4], an unexplored range in all the previous reports.

High-pressure high-temperature in situ X-ray diffraction patterns, here reported for the first time, proved that CO₂-V is the only non-molecular form of CO₂ relevant to the Earth's deep interior. Moreover, contrary to the previous findings, no evidences for the decomposition of CO₂-V into the elements have been found. Variation of the Bragg peak distribution on Debye-Scherrer rings at temperatures >4000 K [4] may suggest a further possible extension of the stability field of this polymeric solid toward the pre-melting state. The presented findings play a pivotal role in understanding the behavior of hot dense carbon dioxide and provide a good basis for further experimental studies of CO₂ at extreme pressures and temperatures.

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