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Swift Heavy Ion Irradiation of Dense GeO2 Glass at Ultrahigh Pressure: Formation and Stabilization of a Disordered NiAs-Type Structure

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Research on materials under coupled extreme conditions including pressure, temperature, and irradiation has become a new and vibrant area of investigation [1]. Incorporation of relativistic ion beams, in particular, has proven effective for synthesis and stabilization of novel phases far from thermodynamic equilibrium [2]. The technique couples static compression and high-density energy deposition via the bombardment of pressurized samples by relativistic heavy ions that are injected into a diamond-anvil cell [3]. Most recently, we applied this technique to amorphous germanium dioxide (GeO2).

Germanium dioxide boasts a diverse array of polymorphs. One hexagonal polymorph, disordered niccolite (d-NiAs-type) GeO2, is notably absent in nature. This d-NiAs-type structure forms exclusively from aperiodic starting materials during shockwave experiments, and static compression experiments in a limited temperature range (1000 – 1300 K) at pressures above 6 GPa [4]. Prior attempts to quench the high-pressure phase were unsuccessful —noting a gradual transformation to the stishovite structure within hours. Here, we report on the crystallization and permanent stabilization of the d-NiAs-type structure of GeO2 formed by in situ irradiation of GeO2 glass with 6 GeV 209Bi ions at 45 GPa in the absence of external heating. Synchrotron x-ray structural refinement of the quenched material suggests that the phase is stabilized by ion-induced cation vacancies that randomly occupy half of the octahedral sites.

References:

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