High Pressure and High Temperature polymorphism of Na_2CO_3 up to 10 GPa

Benedetta CHRAPPAN SOLDAVINI (University of Milan, Italy),
Marco MERLINI (University of Milan, Italy),
Wilson CRICHTON (ESRF, France)

Abstract

Sodium carbonate (Na_2CO_3) is a model system for studying complex polymorphism, owing to its rich sequence of temperature-driven phase transitions [1] and the presence of an incommensurately modulated structure at ambient conditions [2,3,4]. Despite extensive crystallographic investigations, its behavior under high-pressure and high-temperature (HP-HT) conditions remains only partially constrained, particularly in the 0-10 GPa range.

In this study, we present an in-situ investigation of Na_2CO_3 combining single-crystal X-ray diffraction and large-volume press (LVP) experiments to explore its thermoelastic properties and phase stability up to 10 GPa. We identify two previously unreported high-pressure polymorphs, ε and ε-II. The ε phase, stable above ~2 GPa, crystallizes in the monoclinic space group Cc and is characterized by a doubling of the c unit-cell parameter relative to the γ and β polymorphs. Its bulk modulus (47.6(8) GPa) is comparable to that of the γ phase, indicating similar compressibility. The ε-II phase, observed at higher pressures (~11 GPa), likely represents a metastable distorted variant of the ε structure.

By mapping phase transitions across a wide pressure-temperature range and assessing their reversibility, we refine the topology of the Na_2CO_3 phase diagram. Integration of high-precision single-crystal data with LVP constraints allows us to propose an updated phase diagram (Figure 1) featuring an expanded stability field for the incommensurate γ phase and a broad stability region for the ε polymorph under high-pressure conditions.

These findings provide new experimental constraints on the high-pressure behavior of sodium carbonate, improving the reliability of its phase diagram and offering a robust framework for future crystallographic, computational, and high-pressure studies.

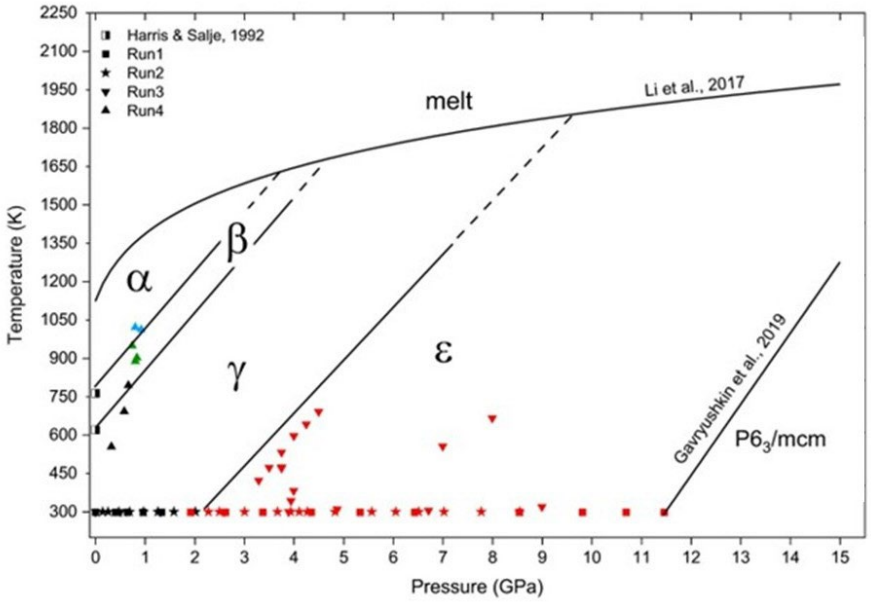

Figure 1: Phase diagram of sodium carbonate obtained from experimental data.

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