

The high-pressure crystal structure of potassium hydrogen carbonate (KHCO₃)

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ABSTRACT

The crystal structure of the high-pressure phase of potassium hydrogen carbonate, here termed KHCO₃ form III, has been solved using single-crystal X-ray diffraction techniques. It adopts triclinic $P\bar{1}$ symmetry and is formed on direct compression of the monoclinic ambient-pressure phase (kalicinite, form I) via a first-order phase transition at 3.2 GPa ($\Delta V/V \sim 4\%$). We have also used time-of-flight high-pressure neutron powder-diffraction to determine the structural changes in KDCO₃ of the form I and III polymorphs to 8.3 GPa. This study indicates that the transition appears to be in response to pronounced displacements of the K⁺ cations and the cooperative tilting of the (DCO₃)₂ dimers. The O···O hydrogen bond distance shows a monotonic compression over the entire pressure range studied with no obvious discontinuity at the phase transition. However, the O-D···O bond angle appears to exhibit an abrupt $\sim 4^\circ$ decrease across the I–III phase transition with a concomitant change in its pressure dependence. Birch Murnaghan fits to the equation of state data above and below the transition indicate that form III [$B_0 = 26.5(2.8)$ GPa, $B' = 5.2(6)$] is marginally less compressible than form I [$B_0 = 22.7(8)$ GPa, $B' = 4.1(5)$].

Keywords: Kalicinite, high-pressure, crystal structure, phase transition