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

D.R. Allan,¹,* W.G. Marshall, ² AND C.R. Pulham¹

¹School of Chemistry and Centre for Science at Extreme Conditions, The University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, U.K. ²ISIS Facility, CCLRC Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, U.K.

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 PT 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 (ΔF/F ≈ 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 ~4° 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 [B₀ = 26.5(2.8) GPa, B’ = 5.2(6)] is marginally less compressible than form I [B₀ = 22.7(8) GPa, B’ = 4.1(5)].

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

INTRODUCTION

The behavior of hydrous mineral phases under conditions of high pressure is of fundamental importance to geological processes occurring in the Earth’s interior. For example, dehydration reactions in subducting slabs are often associated with volcanic activity at the Earth’s surface and with the triggering of deep-focussed earthquakes. Many of the hydrous minerals in subduction zones act as water “sinks,” often containing several wt% of water, and so are of crucial importance to the water budget of the mantle. Minerals such as carbonates and bicarbonates (or hydrogen carbonates) act as sinks for carbon dioxide, and there is increasing interest in these materials as a means of combating global warming by sequestration of the CO₂ produced by the combustion of fossil fuels. Hydrogen bonding plays a pivotal role in the relative structural stability of these minerals and as a consequence a range of high-pressure spectroscopic and diffraction techniques have been used to examine the effect of compression on the hydrogen bond. Among these minerals kalicinite (potassium bicarbonate, KHCO₃) has attracted significant recent attention, not only on account of its relatively simple structure, but also because of the unusually strong hydrogen bonding observed in the structure at ambient pressure. This system is also of more fundamental interest on account of the diffuse scattering observed from single crystals of KHCO₃ at low temperature that has been interpreted in terms of long-range quantum wavefunction entanglement of the indistinguishable protons (Fillaux et al. 2003; Keen and Lovesey 2003; Fillaux and Cousson 2004).

Under ambient conditions KHCO₃ crystallizes from aqueous solution in the monoclinic P2₁/a space group (form I—kalicinite) (Nitta et al. 1952; Thomas et al. 1974). The structure is characterized by the presence of strongly hydrogen bonded (HCO₃)₂ dimers which are disposed on planes parallel to (301). The potassium cations are coordinated to eight oxygen atoms from six HCO₃ anions, and it is this coordination environment which bridges the otherwise isolated dimers. With a relatively short O···O separation of 2.656(4) Å, an H···O distance of 1.64(1) Å and an O-D···O angle of 175.9(6)° (Kagi et al. 2003), the hydrogen bonding within the structure is relatively strong. The hydrogen atoms are all crystallographically equivalent and so their local dynamics can be represented with symmetric pairs of coupled oscillators. At temperatures below ~14 K, in the degenerate ground state, Pauli exclusion imposes proton spin correlation on the hydrogen atoms, which in turn separates their dynamics from those of the other atoms in the structure, resulting in long-range quantum entanglement. This effect has been probed by single-crystal neutron diffraction techniques in KHCO₃ and the resulting diffraction pattern exhibits rods of intensity, superimposed on the P2₁/a structure reciprocal lattice. These features were attributed to a sublattice of protons acting as a regular array of double slits parallel to the dimer planes (Keen and Lovesey 2003), although the full theoretical interpretation of these results has been the subject of some debate (Fillaux and Cousson 2004).

* Present address: Diamond Light Source Ltd., Diamond House, Chilton, Didcot, Oxfordshire, OX11 0DE, U.K. E-mail: David.Allan@diamond.ac.uk