Single-crystal X-ray diffraction study of high-pressure phases of KHCO₃

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ABSTRACT

Monoclinic and triclinic high-pressure phases of KHCO₃ were identified using in situ high-pressure single-crystal X-ray analysis. These monoclinic and triclinic phases, designated as phases IV and V, respectively, differ from three previously identified phases: I–III. The lattices of the two phases are superimposed along a₀* = 2 × a₀ and h0l and h0l nets of both phases lie on the same plane, i.e., the (100) plane is common in both lattices in real space. The space group of phase IV is P2₁/b11 with lattice constants of a = 10.024(3) Å, b = 6.912(5) Å, c = 4.1868(11) Å, α = 115.92(4)°, and V = 260.9(2) Å³. The crystal structure of phase IV, excluding the hydrogen atoms, was successfully determined by direct methods and is isomorphous with a cesium hydrogen carbonate CsHCO₃.

Keywords: KHCO₃, high pressure, single-crystal X-ray diffraction, hydrogen bond

INTRODUCTION

When the donor moiety, X-H, forms a hydrogen bond (H bond) to an acceptor anion Y, i.e., X-H···Y, the potential energy curve becomes broader with shortening of the X···Y distance [d(X···Y)]. For strong hydrogen bonds [d(X···Y)] is ca. 2.5 Å, an asymmetric double minimum develops (e.g., Fig. 1 in Novak 1974), and the barrier between the double minimum potential is reduced as d(X···Y) decreases. In strong hydrogen bonds, in some cases, the proton might transfer from donor to acceptor, i.e., X-H···Y → X-H-Y, a process facilitated by reducing the potential barrier. It is known that the ability of hydrogen bonds to transmit H⁺ (or H₃O⁺) and OH⁻ ions in water or an aqueous medium provides a catalysis mechanism for many reactions (e.g., Jeffrey 1997).

At extremely high-pressure conditions like in the deep Earth, almost all oxide minerals have close packing of oxygen with short d(O–O) to reduce their molar volume. The proton might be included in dense minerals, even those that are nominally anhydrous (Bell and Rossman 1992), resulting in the formation of strong H bonds. Although not often discussed in the Earth science context, proton transfer might play an important role in some physical properties and chemical reactions of minerals, including proton diffusion and hydrolysis in the deep Earth (e.g., Stillinger and Schweizer 1983).

Because of great interest in the dynamic nature of proton transfer, the H bond in potassium hydrogen carbonate KHCO₃ (kalicinite) has been studied using various techniques including X-ray and neutron diffraction methods. In an earlier work, Thomas et al. (1974a, 1974b) showed that the H bond associated with d(O–O) = 2.585(2) Å is moderately strong and that the protons occupy two possible sites in the H bond in the rough proportions of 4:1. In IR and Raman spectra of KHCO₃, the O-H stretching vibration exhibits a broad band between 1800 and 3500 cm⁻¹ (Novak et al. 1963; Lucazeau and Noval 1973). A quasi-symmetric double minimum potential for the proton-stretching mode was proposed to explain the spectroscopic results (Fillaux 1983). A detailed inelastic neutron-scattering study (Ikeda et al. 2002) concluded that anharmonicity plays a major role and that proton dynamics cannot be represented using normal coordinates within the harmonic force-field approximation. Pressure is an attractive tool for understanding proton dynamics because, in principle, the d(O–O) associated with the H bond would decrease with decreasing volume, allowing the anharmonicity to be tuned continuously.

At atmospheric pressure, KHCO₃ undergoes an antiferrodistortive phase transition of an order-disorder type between phase I (Fig. 1a; high-temperature phase, space group: C2/m) and phase II (Fig. 1b; low-temperature phase, space group: P2₁/a) at Tᵢ = 318 K (Kashida and Yamamoto 1990). Two (HCO₃) groups in the crystal are bonded by two H bonds and form (HCO₃)₂ dimers. These dimers have two stable rotational angles around the e axis, which were drawn as right and left-inclined bold lines in Figure 1. These dimers are disordered in phase I and ordered with an anti-phase configuration in phase II.

Recently, new polymorphs of KHCO₃ have been reported by several investigators (Takasaka et al. 2002; Nagai et al. 2002; Kagi et al. 2003, 2005). One of the polymorphs is phase III, which is promoted by shear stress (Takasaka et al. 2002). Although the crystal structure of phase III has not been determined, Kerst et al. (1995) reported the appearance of triclinic ferroelastic domains [space group C1 or C, a = 15.182(3) Å, b = 5.6320(3) Å, c = 3649.28(13) Å, α = 113.7(1)°, β = 100.5(1)°, γ = 102.7(1)°, V = 34942.7(6) Å³, Z = 4].

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