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Study on crystallographically inequivalent protons in RbH_2AsO_4 using static NMR and MAS NMR

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ABSTRACT

Two inequivalent protons from ^1H NMR spectra of RbH_2AsO_4 in the paraelectric phase were distinguished using static NMR and MAS NMR. From the ^1H spin–lattice relaxation times in the laboratory frame, T_1, and rotating frame, $T_{1\rho}$, of the two crystallographically inequivalent hydrogen sites, i.e., H(1) and H(2), the temperature dependences of T_1 and $T_{1\rho}$ for H(1) were related to the reorientational motion. The shorter H(1) bonds give rise to stronger H-bonds, and protons involved in stronger H-bonds have long relaxation times. Consequently, the RbH_2AsO_4 structure has two crystallographically inequivalent sites with two different hydrogen-bond lengths.

1. Introduction

For applications in electrochemical devices such as batteries, sensors, and fuel cells, a solid electrolyte is preferable to a liquid electrolyte. Previously, solid acids were proposed as fuel cell electrolytes [1–3]. AH_2BO_4 (A = K, Rb, Cs, or NH_4; B = P or As) compounds have been suggested for use in fuel cells because they undergo a superionic phase transition at high temperatures [1,2,4,5]. These salts consist of oxyanions such as PO_4 or AsO_4 linked via O–H···O hydrogen bonds. Although considerable effort has been devoted to studying the fast-proton conducting phase in these compounds in the past few years, the exact nature of the transition to that phase is still unknown. This crystal family exhibits a phase-transition-like phenomenon called the high-temperature phase transition at a characteristic temperature T_p. For example, RbH_2AsO_4 undergoes a phase transition at $T_C = 110$ K from a high-temperature paraelectric phase to a low-temperature ferroelectric phase [6–8]. In the paraelectric phase, the crystal has a tetragonal structure with space group I42d, while in the ferroelectric phase, it has an orthorhombic structure with space group Fdd2 [7]. Although many researchers have reported on the high-temperature phase transition in this family, there are significant disparities between the reported T_P values for RbH_2AsO_4 crystals.

Nuclear magnetic resonance (NMR) studies have revealed that RbH_2AsO_4 begins to decompose at 402 K [9]. However, Zhigarnovskii et al. [10] discovered polymorphous transformations at 443 K with the formation of a monoclinic phase that is not observable in differential thermal analysis (DTA) curves; it can only be detected through high-temperature x-ray diffraction analysis. Using another method, i.e., a differential scanning calorimetry (DSC) curve for RbH_2AsO_4, it was determined that the decomposition of RbH_2AsO_4 started at 465 K and spread over ~70 K [11]. Later, Torijano et al. [12] reported that the high-temperature phase transition of RbH_2AsO_4 was observed at T_P ~ 423 K. Recently, DCS results have revealed that this high temperature phase transition occurs near 464 and 478 K for heating rates of 5 and 10 °C/min, respectively [13]. In addition, the ferroelectric–paraelectric phase transition obtained from the ^{87}Rb NMR relaxation time measurements were also recently reported; the ^{87}Rb NMR line at the phase transition temperature T_C (=110 K) splits into two lines, which indicates the occurrence of a phase transition from the tetragonal to orthorhombic phase. Furthermore, the spin–lattice relaxation time in the laboratory frame T_1 for the ^{87}Rb nucleus undergoes remarkable changes near T_C, which indicates drastic alterations of the spin dynamics at T_C [13].

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The spin–lattice relaxation time in the rotating frame $T_{1\rho}$ is similar to that in the laboratory frame T_1. Measurements of $T_{1\rho}$ are advantageous because they investigate the molecular motion in the kHz range, whereas T_1 reflects motion in the MHz range. In this paper, we investigated the temperature dependences of the full width at half maximum (FWHM) in RbH_2AsO_4 using static NMR and magic angle spinning (MAS) NMR experiments. Furthermore, the spin–lattice relaxation times in the laboratory frame T_1 and in the rotating frame $T_{1\rho}$ are measured as functions of temperature. In particular, the well-separated single-crystal NMR and MAS NMR line components of the crystallographically inequivalent proton sites in RbH_2AsO_4 have provided us with a unique opportunity to study the distinct proton dynamics associated with the different hydrogen-bond lengths. NMR behaviors of the two inequivalent proton sites in RbH_2AsO_4 are discussed in this work.

2. Crystal structure

RbH_2AsO_4, with $T_C = 110$ K is orthorhombic in the ferroelectric phase and belongs to the high-temperature paraelectric phase of the space group I42d. The lattice constants of tetragonal at room temperature are $a = 7.7865$ Å, $c = 7.466$ Å, and $Z = 4$ [14]. The AsO_4 tetrahedral groups are linked by two hydrogen bonds, forming zigzag chains along the *a*- and *b*-axis, as shown in Fig. 1. The hydrogen bond H(1), with a connection to the Rb atom, appears to be stronger with a shorter bond length, whereas the H(2) forms a longer hydrogen bond length with the oxygen atom, which is bonded to a As atom [15]. The Rb^+ cations are located in channels running along the *a*-directions and are coordinated by eight O atoms located at the vertices of a snub disphenoid. In addition, the Rb ion in the ferroelectric phase exists at two Rb^+ sites per unit cell.

3. Experimental method

The NMR spectrum and spin–lattice relaxation times in the laboratory frame T_1 for ^1H nuclei in RbH_2AsO_4 single crystals were measured using a Varian 200 MHz NMR spectrometer at the Korea Basic Science Institute. The static magnetic field was 4.7 T, and the central radio frequencies were set to $\omega_o/2\pi = 200$ MHz for the ^1H nuclei. Here, the crystal orientation with respect to the magnetic field was along the crystallographic c-axis. The ^1H T_1 measurement was performed using $\pi - t - \pi/2$ pulse sequences. The nuclear magnetization S(t) of the ^1H nuclei at a time *t* after the π pulses were determined from the inversion recovery sequence following each pulse. The width of the $\pi/2$ pulse was 2.8 μs for ^1H.

To obtain the NMR spectrum and spin–lattice relaxation times in the rotating frame $T_{1\rho}$ for ^1H nuclei in RbH_2AsO_4, MAS NMR experiments were performed using a Bruker 400 MHz NMR spectrometer at the Korea Basic Science Institute. The ^1H MAS NMR experiments were performed at a Larmor frequency of $\omega_o/2\pi = 400$ MHz. A powdered sample was placed in the 4 mm MAS probe, and the MAS rate was set to 10 kHz to minimize the spinning sideband overlap. The ^1H spin–lattice relaxation time in the rotating frame $T_{1\rho}$ was measured by varying the length of the spin-locking pulses. The $\pi/2$ pulse width used for $T_{1\rho}$ was 5 μs according to the spin-locking field strength of $\omega_1 = 50$ kHz. The NMR measurements were obtained in the temperature range of 180–430 K.

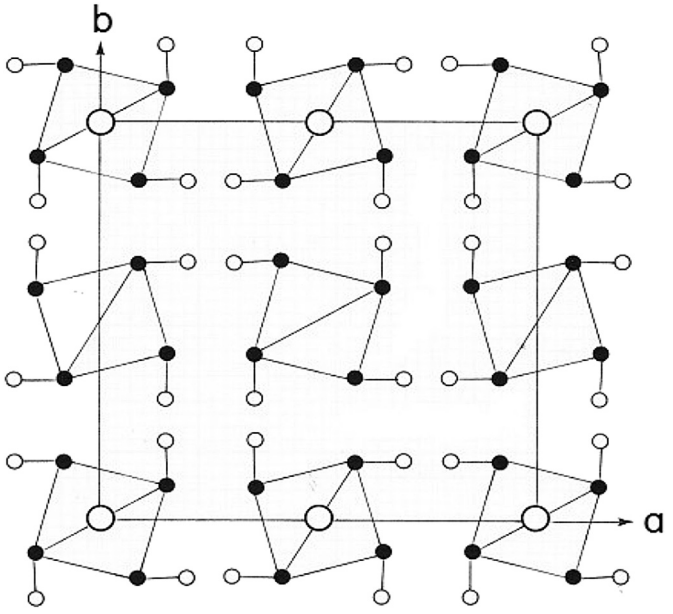

Fig. 1. The crystal structure of RbH_2AsO_4 in the paraelectric phase on the *ab*-plane. The AsO_4 tetrahedron, Rb, O, and H atoms are indicated by the big square, large open circle, dark circle, and small open circle, respectively.

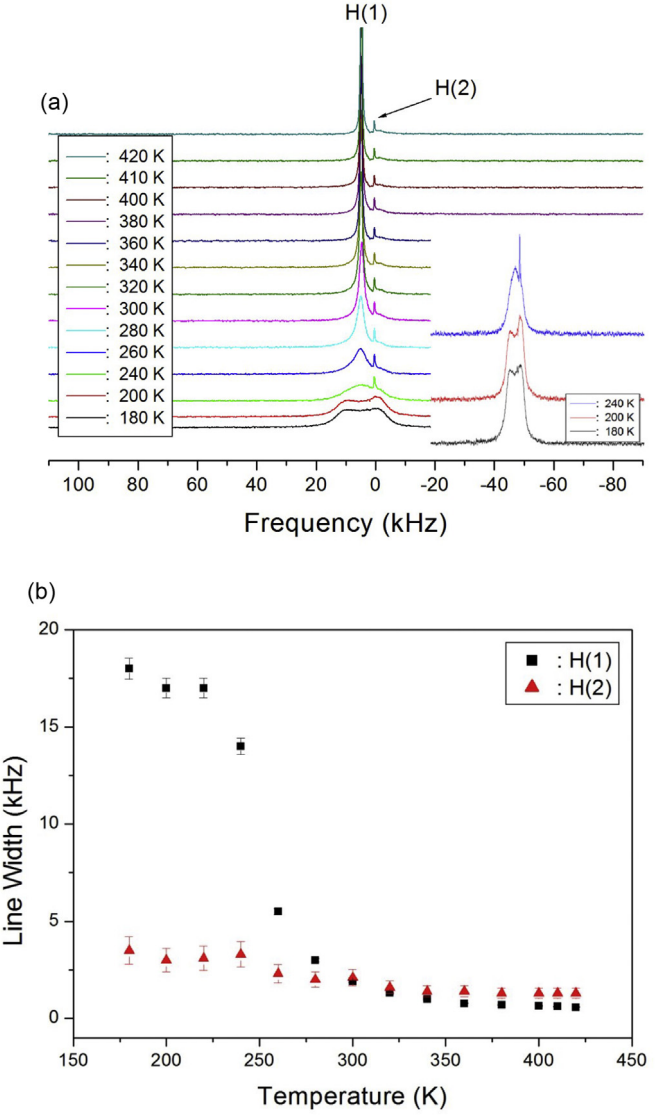

Fig. 2. (a) Temperature dependences of the ^1H NMR spectrum in a RbH_2AsO_4 single crystal and (b) Line widths of H(1) and H(2) for a RbH_2AsO_4 single crystal as functions of temperature.