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Proton dynamics in ZnO nanorods: An NMR study

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The rotating-frame spin-lattice relaxation of two types of the hydrogen donors was well distinguished in the 1H nuclear magnetic resonance (NMR) measurements, providing a unique opportunity to study the distinct proton dynamics in ZnO nanorods. NMR relaxometry is a powerful technique of atomic-scale access to probe ion hopping motion in solids. The laboratory-frame relaxation rate is effective for probing nuclear spin processing in radio frequency range, i.e., fast diffusing spins. The rotating-frame relaxation rate, on the other hand, effectively probes motions occurring at ultralow-frequencies. While spin-lattice relaxation in the laboratory-frame showed a single-exponential form presumably due to spin mixing by spin diffusion, the spin-lattice relaxation in the rotating-frame showed a well-resolved double-exponential form, allowing us to distinguish the dynamics of the two distinct proton species in ZnO synthesized at relatively low-temperature of 573 K. Here, we demonstrate that the conversion from interstitial H (Hi) to oxygen-substitution H (HO) in ZnO dynamically takes place at elevated temperatures by means of the 1H NMR. The activation barriers for migration of Hi and for binding of Hi with an oxygen vacancy to form HO are revealed to be 0.27 eV and 0.51 eV, supporting those obtained by ab initio calculations. In proton-implanted ZnO, we identify comprehensive hydrogen species and investigate their dynamical properties. Unlike in unirradiated sample, after irradiation mobile protons at the interstitial site were observed in the systems synthesized at relatively high-temperature of 773 K. The activation energy obtained was 0.46 eV by the Arrhenius relation, corresponding to that of long-range hopping motion. Multiple NMR lines at ~1 ppm, assigned to the hydroxyl group were observed and their diffusion properties have been investigated before and after irradiation. Our work gives manifest evidence for the first time from a microscopic point of view that implanted protons become mobile in the lattice.

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