Research Group for Nanoscale Structure and Function of Advanced Materials

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The research objective of Nanoscale Structure and Function of Advanced Materials group is to study nanoscale structures of functional devices and materials under external fields by using high-intensity quantum beams of muons, positron, neutron, and synchrotron light. As a highlighted result in our group, an atomic configuration of germanene, *i.e.*, a single layer of germanium, is experimentally revealed to have an asymmetric sheet structure by Total-Reflection High-Energy Positron Diffraction method [1]. The phase separation near a metal-insulator transition of Mott system has been revealed as an international collaboration of REIMEI research by using positive muon spin rotation/relaxation spectroscopy (μ^+SR) [2]. In this activity report, our recent progress in the research of a mixed electron/hydrogen ion conductor with microscopic insights into hydrogen transport is described from a unique approach using μ^+SR.

Excited configurations of hydrogen in the $BaTiO_{3-x}H_x$ perovskite lattice associated with hydrogen exchange and transport [3]

Oxyhydrides of perovskite titanates $ATiO_{3-x}H_x$ (*A*=Ba, Sr, Ca) have attracted much attention because of their fascinating properties, which are associated with the lability of H^- ions [4]. These are obtained as O^{2-}/H^- solid solutions and can contain a large amount of hydrogen up to x~0.6. Macroscopic gas analysis revealed that the hydrogen is mobile and exchangeable in its gaseous environment at temperatures above 400 °C. The H substitution changes the parent band insulators into paramagnetic metals, as evidenced by electrical resistivity and magnetic susceptibility measurements. These transport and hydrogen exchange characters make these materials potentially suitable for application in mixed electron/hydrogen ion conductors and hydrogen membranes. However, experimental insights into the hydrogen dynamics in the $ATiO_{3-x}H_x$ lattice are still quite limited.

In this study, we investigated excited configurations of hydrogen anions in $BaTiO_{3-x}H_x$ (x=0.1–0.5) by μ^+SR spectroscopy, which have been predicted from a computational study to be involved in its hydrogen transport and exchange processes [5]. In standard μ^+SR measurements, spin-polarized positive muons with a kinetic energy of ~4 MeV are implanted into a solid-state specimen and the energy is lost mainly by ionization. They are then trapped at local potential minima, not necessarily at the global minimum. Finally, the electronic structure of muonium (a hydrogen-like μ^+–e^- bound state: Mu) or its ionized species (Mu^+ or Mu^-) is probed by the μ^+SR technique, which is supposed to be very similar to that of hydrogen. In general, the as-implanted mixture of Mu states is far from equilibrium and can involve metastable excited states [6]. Therefore, the μ^+SR method is suitable to obtain microscopic insights into excited configurations of hydrogen in the $BaTiO_{3-x}H_x$ lattice.

Positive muons implanted into the powder samples of $BaTiO_{3-x}H_x$ were mainly found in two metastable states. One was assigned to a highly mobile interstitial protonic state as illustrated in Fig. 1(a), which is often observed in perovskite oxides. The other was found to form an entangled two spin-1/2 system with the nuclear spin of H^- ion in the host lattice as shown in Fig. 1(b). The structure of the (H, Mu) complex agrees well with that of a neutralized center containing two H^- ions at an oxygen vacancy V_O^{2+}, which was predicted to form in oxygen-deficient $SrTiO_{3-\delta}$ from another computational study [7]. These observations are mostly in line with a theoretical proposal on hydrogen transport and exchange involving charge-state transitions [5,7,8]. In addition, we observed interstitial Mu^+ diffusion and re-trapping at a deep defect above 100 K as evidenced from the temperature dependence of a muon spin relaxation rate associated with the interstitial Mu^+ component. This could be a rate-limiting step of macroscopic Mu/H transport in the $BaTiO_{3-x}H_x$ lattice.

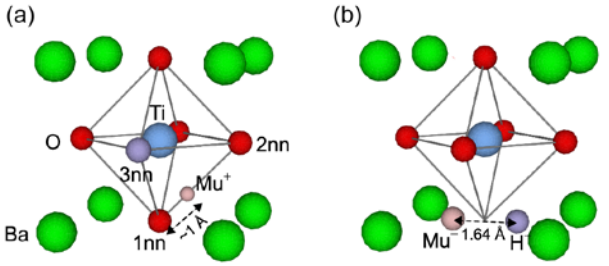

Fig. 1. (a) Atomic configuration for the highly mobile interstitial Mu^+. The first and second nearest neighbour anion sites (1 nn and 2 nn) are fixed to be O^{2-} and the third nearest neighbour (3 nn) and further anion sites are randomly replaced with H^- with a probability of x/3. (b) Atomic configuration for the (H^-, Mu^-) complex at an oxygen vacancy, where hydrogen exchange can occur.

References

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