

博士論文の要約

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論文題目 Effects of Compositions and Sintering Process on Phase Transition Behavior and Hydride Ion Conducting Property in K_2NiF_4 -type Ba-Li Oxyhydride

Hydrogen transport in solids is crucial in electrochemical devices, such as fuel cells, gas sensors, and batteries. The recent verification of the hydride ion (H^-) diffusion in solids^[1] and the demonstration of the potential battery reaction based on H^- conduction^[2] have led to the recognition of H^- as a new charge carrier of hydrogen. The low charge density (monovalence and moderate size) and high polarizability of H^- are advantageous for fast diffusion in solids, while strong reducing ability (-2.23 V vs. SHE) should be effective for high activity in energy conversion and high energy density in batteries. H^- conductors are an emerging class in the field of solid state ionics. In the study of H^- conductors, oxyhydrides are currently the primary targets of materials exploration because coexisting oxide and hydride ions have facilitated the control of the H^- concentration and anion arrangement, which are essential for forming a smooth H^- diffusion pathway. Outstanding materials, such as $Ba_{2-x-y}LiH_{3-2x}O_{1-y}$ ($x = 0.15$, $y = 0.1$), which exhibit practical conductivities over $10^{-2} S \cdot cm^{-1}$ above 315 °C, have been reported so far.^[3] However, applying H^- conduction to energy/material conversion requires solid electrolytes that can operate in a wide range from room temperature to intermediate temperature (~ 400 °C), and further progress in material development is needed.

K_2NiF_4 -type $Ba_{2-x-y}LiH_{3-2x}O_{1-y}$ (hereafter called BLHO) exhibiting high conductivity above $10^{-2} S \cdot cm^{-1}$ with extremely low activation energy is the first hydride ionic conductor that can be classified as a so-called superionic conductor (**Figure 1**). BLHO has a stable composition of the highly vacant $Ba_{1.75}LiH_{2.7}O_{0.9}$ ($x = 0.15$, $y = 0.1$) under ambient pressure and forms the superlattice structure at low temperature (β -BLHO, space group: $Pnm2_1$) due to three types of long-range ordering, namely H_{eq}/V_H , H_{ap}/O_{ap} and Ba/V_{Ba} (H_{eq} , O_{ap} and V_M represent hydrogen at

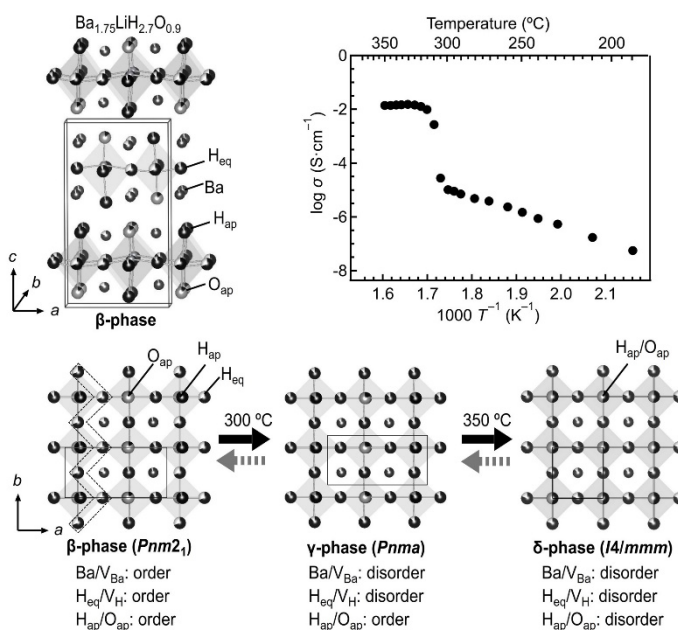


Figure 1. Changes in the crystal structure and H^- conductivity for $Ba_{1.75}LiH_{2.7}O_{0.9}$ with elevating temperature^[3].

equatorial anion sites, oxygen at apical anion sites, and a vacancy at M sites, respectively). These long-range orders are successively lost upon heating, transforming to γ -BLHO (space group: $Pnma$) at 300 °C, where only the H_{ap}/O_{ap} ordering remains, and to δ -BLHO (space group: $I4/mmm$) at 350 °C, where all long-range orderings are disordered. The H^- conductivity enhances after β - γ phase transition to the superionic conduction state.

In this study, the effects of elemental substitution and sintering were verified to stabilize the superionic conduction phase of BLHO to lower temperatures. For the former case, I synthesized solid solutions in which Li and Ba were partially substituted by Na and K, respectively, and investigated the effects of these elemental substitutions on the crystal structure, and thus on the phase transition behavior and the H^- conductivity. In the latter case, sintered BLHO with improved relative density was prepared by hot pressing.

For the Na solid solutions (Na-BLHO), crystal structure analysis at room temperature (RT) suggested lowering the degree of long-range ordering of H_{cq}/V_H and Ba/V_{Ba} , meaning the anion arrangement of Na-BLHO at room temperature resembles that of the superionic conducting phase (γ -BLHO). The transition enthalpy change estimated by DSC measurement decreased with increasing Na content. As a result of electrochemical impedance spectroscopy (EIS), the conductivity below 300 °C for the composition of $x \geq 0.4$ (40% Na/Li) increased over 100 times (Figure 2: $x = 0.6$). Additionally, the slope of discontinuous transitions to the high conductivity region due to phase transition became shallower, implying that the transition behavior to the superionic phase for Na solid solutions was altered from BLHO.^[4]

For the K solid solutions (K-BLHO), the structural refinements at RT, 270 °C, and 430 °C suggested that K-BLHO also remains the same three types of long-range ordering as that of β -BLHO at RT, except for introducing H^- vacancies at the apical site on the Li-anion octahedra due to charge compensation. At 270 °C, it was found that K-BLHO had already transformed to the γ -phase. As a result of EIS measurements, the phase transition temperatures were decreased by approximately 50 °C via 15% K/Ba substitution, resulting in a high conductivity at lower temperatures (Figure 2: $y = 0.3$).^[5]

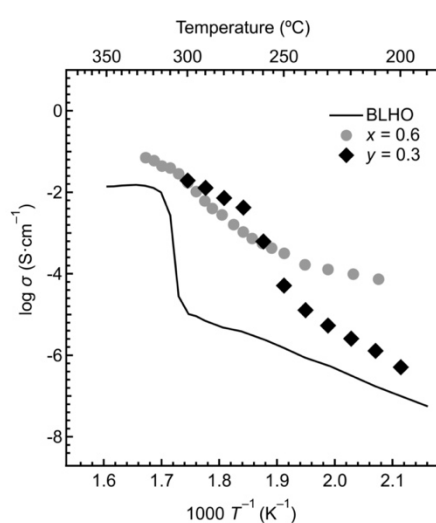


Figure 2. The Arrhenius plots of H^- conductivity of $Ba_2Li_{1-x}Na_xH_3O$ (Na-BLHO) and $K_yBa_{2-y}LiH_{3-y}O$ (K-BLHO).

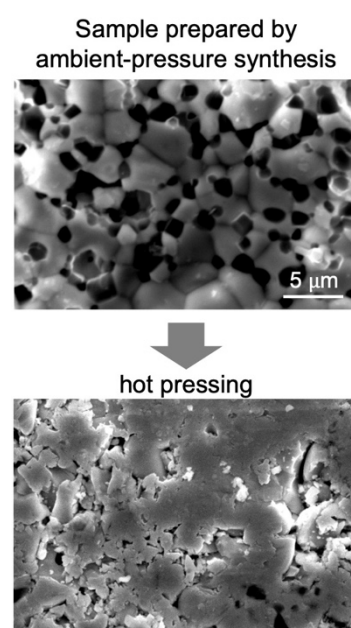


Figure 3. The SEM images of the samples before and after hot pressing.

The relative density of BLHO was successfully improved to 97% from ca. 80% by hot pressing at 450 °C after pulverization of the pellets prepared by conventional ambient-pressure synthesis. SEM observation of the surface of the pellet showed that the hot-pressed one advanced densification, whereas as prepared one had many voids (Figure 3). This sintering condition for fabricating dense pellets is significantly low compared to common oxide-based solid electrolytes, which require sintering above 1000°C. The high diffusivity of H⁻ and “softness” resulting from high polarizability might affect good sinterability.

This study reveals that the Na and K substitutions in BLHO are effective in stabilizing the superionic conduction phase and suggests that the control of morphology and density are important to improve the performance of BLHO as solid electrolytes. It is particularly interesting that the elemental substitutions of Na and K results in the different anion arrangements at room temperature. There remains room for further performance improvements, such as optimizing substituted species and their concentrations, multi-element substitution, and tuning morphology for pellets, and thus stabilizing the highly conductive phase of BLHO would be a principal guideline for developing hydride ion conductors.

References

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