

Absence of an expected structural transition in the H^- conductor $\text{A}_2\text{H}_3\text{X}$

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Recently, hydride ion (H^-), a negative hydrogen ion, is promising as a next generation of hydrogen carriers due to its favorable properties for ionic conduction, including a monovalent formal charge, high redox potential (-2.23 V vs. SHE), and large polarizability. We have found that hydride conductors $\text{Ba}_2\text{H}_3\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), prepared under ambient pressure, adopt a high symmetric hcp framework of Ba^{2+} similar with that of the high temperature phase of BaH_2 and exhibit high H^- conductivity below 300 °C [1]. In contrast, the ionic conductivity of $\text{A}_2\text{H}_3\text{X}$ obtained by high-pressure synthesis was about $10^{-5} - 10^{-7}$ S/cm in the low-temperature region below 620 K. Above 620 K, however, the ionic conductivity increased rapidly, reaching 10^{-3} S/cm. This discontinuous behavior in ionic conductivity was reversible with respect to temperature change, indicating that it is not likely to be decomposition due to hydrogen release. This jump behavior of H^- conductivity is an important observation in the development of H^- conductors. To elucidate this transition behavior, high temperature neutron powder diffraction (NPD) measurements were performed on $\text{A}_2\text{H}_3\text{X}$ prepared under high pressure.

The NPD experiments were carried out on deuterated samples. First, a sample was measured at five temperatures (300K , 373K , 473K , 623K , and 653K) using a high-temperature controller during the heating process. Then, measurements were performed during the cooling process.

Figure 1 shows the NPD patterns of $\text{A}_2\text{H}_3\text{X}$ at several temperatures. Some of peaks were indexed using a hexagonal lattice. However, already in the room temperature NPD pattern, there were several peaks that could not be indexed with the hexagonal lattice and possible impurities. Perhaps they might originate from a superlattice specific to the $\text{A}_2\text{H}_3\text{X}$ prepared

under high pressure (compared with $\text{A}_2\text{H}_3\text{X}$ synthesized at ambient pressure), but at this stage we have not yet reached an identification. In all temperature ranges examined, the lattice parameter increased linearly with increasing temperature. No significant peaks change in the NPD patterns was observed above the phase transition temperature suggested by ionic conduction measurements. This result suggests that the observed conductivity jump $\text{A}_2\text{H}_3\text{X}$ might be a transition without a structural change. However, there was a problem with the installation of the sample tube in the temperature controller and the actual sample temperature may not have exceeded 620 K, at the time of the measurements. Furthermore, given that structurally-related BaH_2 exhibits a steep change in ionic conduction accompanied by a structural phase transition, it is difficult to conclude the presence or absence of a structural phase transition based solely on the results of the NPD measurements.

[1] H. Ubukata *et al.*, *Sci. Adv.* **7**, eabf7883 (2021).

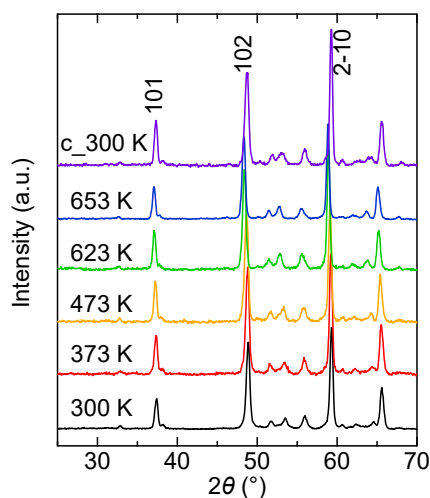


Fig. 1. Neutron diffraction patterns of $\text{Ba}_2\text{H}_3\text{Cl}$ at several temperatures, which were indexed with a hexagonal lattice.