Concentration and site of hydride ion carriers in perovskite metal oxyhydrides

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1. Introduction

Metal oxyhydrides, including the hydride anion (H^-), are rare but have recently become appealing hydrogenation catalysts for ammonia synthesis[1-3] and CO_2 conversion[4, 5]. H^- is simply the counter form of H^+, but the electrochemical activity of the former could clearly be distinguished from that of the latter because the high redox potential of H_2/H^-, at −2.3 V versus a normal hydrogen electrode, may facilitate electron donation to adsorbed molecules.[2, 6] The oxyhydrides must be also important H^- ion conductors because the large polarizability and extraordinary ion-size flexibility of H^- anion is advantageous for the long-range diffusion. In a recent year, cubic perovskite oxide $BaZr_{0.5}In(III)_{0.5}O_{2.75}$ transforms to highly-anion deficient oxyhydride $BaZr_{0.5}In(II)_{0.5}O_{2.25}H_{0.5}$ by annealing at 800°C in a H_2 atmosphere, as given by the consecutive reaction of In reduction ($BaZr_{0.5}In(III)_{0.5}O_{2.75}$ + 0.5 H_2 → $BaZr_{0.5}In(I)_{0.5}O_{2.25}$ + 0.25 H_2O) and oxidative hydrogenation ($BaZr_{0.5}In(I)_{0.5}O_{2.75}$ + 0.25 H_2 → $BaZr_{0.5}In(II)_{0.5}O_{2.25}H_{0.5}$). The resultant $BaZr_{0.5}In_{0.5}O_{2.25}H_{0.5}$ exhibits remarkable H^- ion conductivity, together with electronic conductivity, because the relatively large oxygen deficiency allows fast diffusion of H^- ion by hopping along the nearest neighboring anion sites. Based on these results, it is presumed that the In-rich side $BaZr_{1-x}In_xO_{3-x/2}$ family involve more H^- anion through the reductive hydrogenation and thus the resultant phase exhibit high H^- ion conductivity since the reduction of In atoms may forms more oxygen deficiency. In this study, the structure refinement of $BaZr_{1-x}In_xO_{3-x/2-y}H_z$ family (x =0.4, 0.7) was conducted by neutron diffraction Rietveld analysis so as to determine the H^- anion occupancy in anion and interstitial sites.

2. Experiment

A single phase of cubic perovskite $BaZr_{1-x}In_xO_{3-x/2-y}$ was prepared by solid phase synthesis. $BaZr_{1-x}In_xO_{3-x/2-y}$ powders were annealed in H_2 at appropriate temperature for 24 h and thus isomorphous $BaZr_{1-x}In_xO_{3-x/2-y}H_z$ oxyhydrides were available. Finally, $BaZr_{1-x}In_xO_{3-x/2-y}D_z$ was prepared by D-substitution of $BaZr_{1-x}In_xO_{3-x/2-y}H_z$ with annealing in 20%−D_2/Ar gas at appropriate temperature for 12 h. Neutron diffraction patterns of $BaZr_{1-x}In_xO_{3-x/2-y}D_z$, measured at *iMateria*, were analyzed by Rietveld method with a Z-Riet software.

3. Results

Rietveld profiles of $BaZr_{0.3}In_{0.7}O_{3-x/2-y}D_z$ (H-BZI37) oxyhydride are shown in Figure 1 and the refined structural parameters are summarized in Table 1. The fitting quality factors R_{wp}, R_p and s are significantly decreased to 5.047, 3.221 and 1.998%, respectively, confirming the Rietveld refinement was conducted well. The fitting was first started by fixing the oxygen occupancy at the values determined from the thermogravimetry (TG) measurements, and thus, the occupancy of D in anion site (D_O) and interstitial site (D_i). Secondary, the occupancy of D_O and D_i was fixed and thus the occupancy of O was relaxed.

The structure was refined by repeating these steps. The resultant population of O was 2.157, which remained near the values determined by TG (2.14).

The concentration of D_i in H-BZI46 is near 0 and that of D_O equals to xx, which is smaller than the corresponding value of H-BZI55. The concentration of D_i and D_O in H-BZI64 are both 0, indicating that Zr-rich side $BaZr_{1-x}In_xO_{3-x/2-y}$ is not favorable to form hydride ion in the high p_{H2} atmosphere. The current results demonstrate that the appropriate In contents are required to incorporate amounts of hydride ion in barium indate zircoate perovskite family.

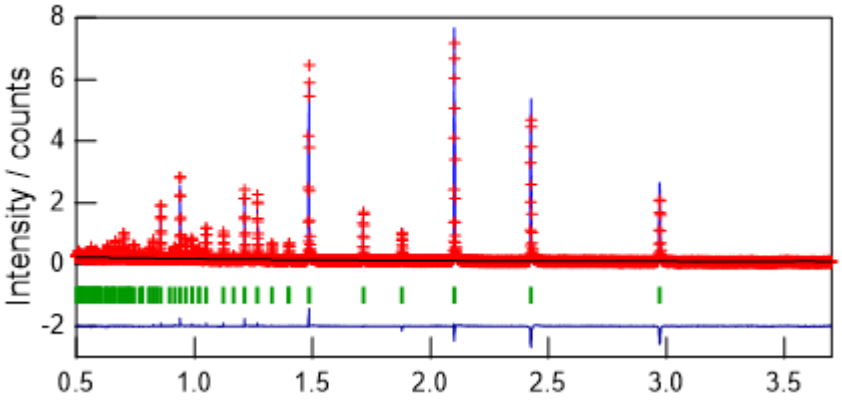

Fig. 1 Rietveld profile of H-BZI37. R_{wp} = 5.047%, s = 1.998%, and R_p = 3.221%.

Table 1 Refined structure parameters of H-BZI37

a / Å	$g(O_O)$	$g(H_O)$	$g(H_i)$	Chemical Composition
	0.7191 ± 6	0.0496 ± 6	0	$BaZr_{0.3}In_{0.7}O_{2.157}D_{0.149}$

4. Conclusion

In summary, it is demonstrated that the concentration of hydride anions in $BaZr_{1-x}In_xO_{3-x/2-y}H_z$ oxyhydride perovskites are strongly dependent on the In contents. z changes from 0 to 0.5 to 0.15 with increasing x from 0.4 to 0.5 to 0.7. The reason for the high hydride anion contents in x = 0.5 phase would be investigated further.