Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Synthesis and Conductivity of New Oxyhydride Ba2YHO3 with H−-rich Rock-salt Layers

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Supporting Information

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Experimental details

Synthesis. Polycrystalline samples of Ba_2YHO_3 oxyhydride were synthesized by solid state reaction under high pressure, using BaH_2 (Mitsuwa Chemical, 99.5%), BaO (Aldrich, 99.99%), Y_2O_3 (Aldrich, 99.999%), and NaH (Aldrich, 95%). The reagents were weighed in an Ar filled glovebox, thoroughly mixed in a planetary ball mill, and sealed in a NaCl capsule inside a pyrophyllite cell with a graphite heater. The cell was heated at 700–1000 °C under 2–4 GPa for 1 h.

Characterization. Structural characterization of the samples was carried out with an X-ray powder diffractometer (Miniflex600, Rigaku) with Cu-Kα radiation. Since the oxyhydride compounds were highly air-sensitive, the powder samples were loaded on an aluminum holder in an Ar filled glovebox. Synchrotron X-ray diffraction (SXRD) data was collected at room temperature using a high-resolution angle-dispersive type X-ray diffractometer (BL02B2) installed at SPring-8. The wavelength of the incident beam was 0.8 Å. The powder samples were sealed in a Lindemann glass capillary (ϕ 0.3 mm) that was rotated during the measurement to reduce the preferential orientation. Neutron diffraction (ND) measurement at room temperature was carried out using a time-of-flight (TOF) neutron SPICA powder diffractometer installed at J-PARC. Powder samples were loaded in a cylindrical vanadium cell. RIETAN-FP and Z-Rietveld programs[1,2] were used to refine the SXRD and ND data, respectively. Crystal structures were illustrated using VESTA software[3]. Thermogravimetric analysis (TGA) was conducted under flowing Ar gas (100 mL/min) with a Rigaku Thermo plus EVO2 installed in an Ar-filled glove box.

First-principles calculations. First-principles total energy calculations were performed using the projector augmented wave method[4,5] as implemented in the VASP code[6–8]. Exchange-correlation interactions of electrons were treated using the Perdew-Burke-Ernzerhof functional (PBE) based on the generalized gradient approximation (GGA)[9]. Configurations of the valence electrons in the PAW potentials are $5s^2\ 5p^6\ 6s^2$ for Ba, $4s^2\ 4p^6\ 4d^1\ 5s^2$ for Y, $2s^2\ 2p^4$ for O, and $1s^1$ for H. The cut-off energy for plane-wave basis sets was set to 500 eV. Lattice constants and atomic internal positions were fully optimized until all residual forces acting on atoms were less than 0.02 eV/Å. Symmetrically independent H/O configurations were identified using the Spglib library[10]. Brillouin-zone integration was performed with Monkhorst Pack grids[11] and k-point spacings less than 0.4 $Å^{-1}$.

Conductivity. Ionic conductivity of the oxyhydrides was measured by the AC impedance method using a pellet sample obtained by high pressure synthesis. The diameter (r) and thickness (t) of measured pellets were r = 3.95 mm and t = 1.35 mm. The sample was coated with molybdenum electrodes sputtered on both sides under H_2 gas flow. The data was collected during heating and cooling cycles at the temperature range of 180–400 °C with an applied frequency range of 0.1 Hz to 35 MHz using an MTZ-35 frequency response analyzer. EC-Lab software was used to fit the spectra with electrically equivalent circuits. The DC electric conductivity of Ba_2YHO_3 was performed at 320 ºC under flowing H_2 gas using the sintered pellet with hydrogen blocking Mo electrodes.

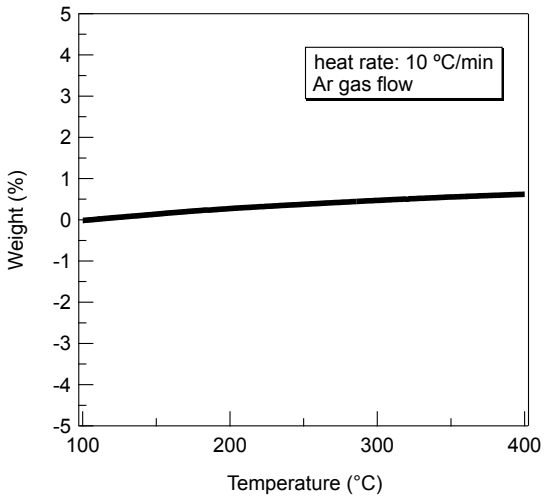

Figure S1. Thermogravimetric analysis (TGA) of Ba_2YHO_3 in heating under flowing Ar gas. The weight loss corresponding to hydrogen loss was not observed.

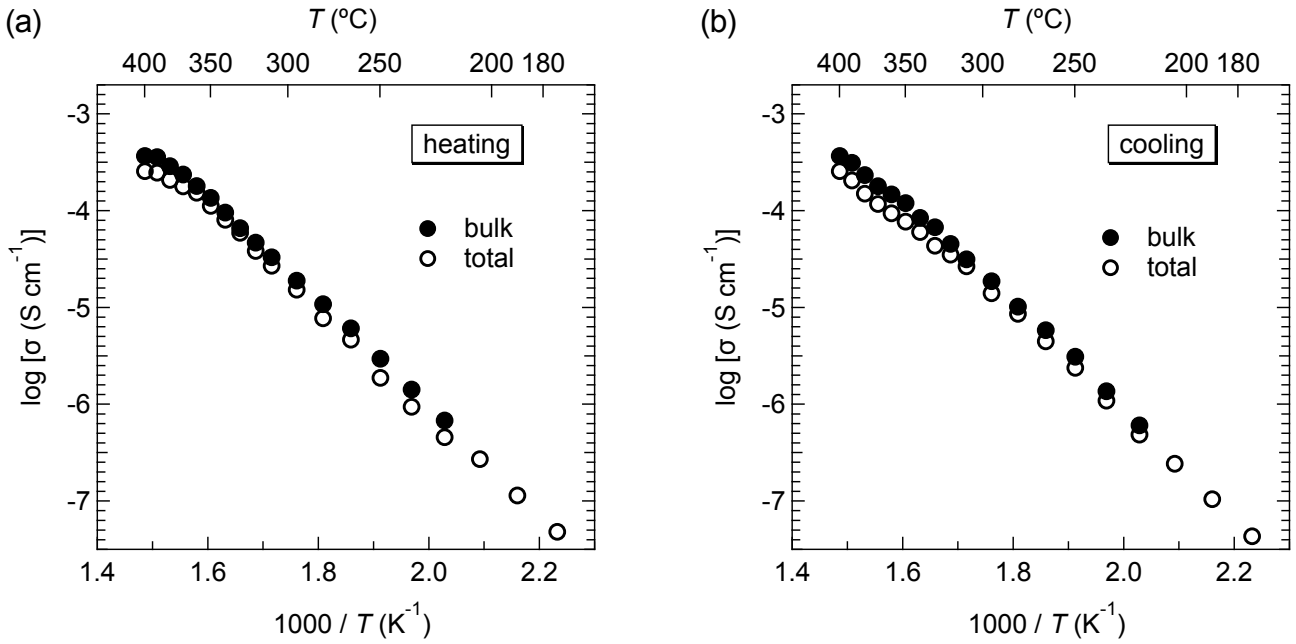

Figure S2. Arrhenius plots of the bulk and total (bulk + grain boundary) conductivity of Ba_2YHO_3 in (a) heating and (b) cooling.

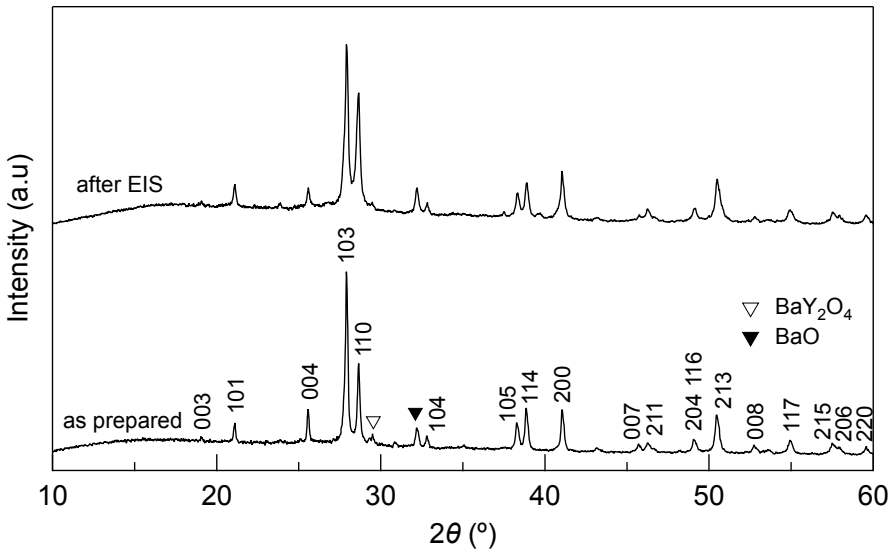

Figure S3. Laboratory XRD profiles of Ba_2YHO_3 before and after electrochemical impedance measurement.

Table S1. Structural parameters of Ba_2YHO_3 from SXRD data collected at room temperature.

atom	site	*g*	*x*	*y*	*z*	*B* /Å^2
Ba(1)	2*c*	1	0.25	0.25	0.37513(6)	0.60(2)
Ba(2)	2*c*	1	0.25	0.25	0.09959(7)	0.99(2)
Y	2*c*	1	0.25	0.25	0.23778(13)	0.32(3)
O(1)	2*c*	1	0.75	0.75	0.0849(7)	3.9(3)
O(2)	4*f*	1	0.75	0.25	0.2666(4)	1.00(13)

*P*4/*nmm*; a = 4.38036(2) Å, c = 13.8234(1) Å.

R_{wp} = 7.26%, R_p = 5.52%, R_e = 4.29%, S = 1.69, R_B = 2.65%, R_F = 0.92%.

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