# Electronic Supporting Information (ESI) High Proton Conductivity in Nb<sup>5+</sup>-doped BaScO<sub>2.5</sub>

## Kei Saito,<sup>a</sup> Mitsuki Baba,<sup>a</sup> Kensei Umeda,<sup>a</sup> Kotaro Fujii,<sup>a</sup> Takashi

## Honda,<sup>b,c</sup> Masatomo Yashima<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, School of Science, Institute of Science Tokyo, 2-12-1-W4-17, O-okayama, Meguro-ku, Tokyo 152-8551, Japan

<sup>b</sup> Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan

<sup>c</sup> J-PARC Center, High Energy Accelerator Research Organization (KEK), Tokai, Ibaraki, 319-1106, Japan

\* Corresponding author: <a href="mailto:yashima@chem.sci.isct.ac.jp">yashima@chem.sci.isct.ac.jp</a>

#### **Methods Section**

Partially hydrated BaSc<sub>1-x</sub>Nb<sub>x</sub>O<sub>2.5+x</sub> (x = 0.20, 0.25, 0.35, 0.45) samples [= BaSc<sub>1-x</sub>Nb<sub>x</sub>O<sub>2.5+x-v/2</sub>(OH)<sub>v</sub>] were prepared by the solid-state-reaction method. Here, x is Nb content and y is proton concentration in  $BaSc_{1-x}Nb_xO_{2.5+x-v/2}(OH)_v$ . We refer  $BaSc_{0.8}Nb_{0.2}O_{2.7-\nu/2}(OH)_{\nu}$ to BSN20 for x = 0.20,  $BaSc_{0.75}Nb_{0.25}O_{2.75-\nu/2}(OH)_{\nu}$  to BSN25 for x = 0.25,  $BaSc_{0.65}Nb_{0.35}O_{2.85-\nu/2}(OH)_{\nu}$  to BSN35 for x = 0.35,  $BaSc_{0.55}Nb_{0.45}O_{2.95-\nu/2}(OH)_{\nu}$  to BSN45 for x = 0.45. Raw materials BaCO<sub>3</sub> (Kojundo Chemical Laboratory Co., 99.95%), Sc<sub>2</sub>O<sub>3</sub> (Shin-Etsu Chemical Co., 99.99%), and Nb<sub>2</sub>O<sub>5</sub> (Kojundo Chemical Laboratory Co., 99.99%) were mixed and ground in an agate mortar for ~1 h as ethanol slurries and as dried powders. The powders thus obtained were calcined in static air at 900 °C for 12 h. The calcined powders were ground into fine powders in the agate mortar for  $\sim 1$  h as ethanol slurries and as dried powders. The fine powders were uniaxially pressed into pellets at ~150 MPa and then sintered in static air at 1600 °C for 10~20 h on an alumina boat. The sintered products were crushed with a tungsten carbide crusher, ground with the agate mortar for  $\sim$ 1 h as ethanol slurries and as dried powders. The obtained samples were uniaxially pressed into pellets at ~150 MPa, isostatically pressed into pellets at ~200 MPa, and sintered in static air at 1600 °C for 10~20 h on the alumina boat. The relative densities of the sintered pellets of BSN25, BSN35, and BSN45 were 70~80%. The sintered pellets of BSN25 were used for the impedance and direct current (DC) electrical conductivity measurements and scanning electron microscope (SEM) observation. The sintered pellets of BSN35 and BSN45 were used for the impedance measurements. Parts of the sintered BSN20, BSN25, BSN35, and BSN45 pellets were crushed and ground into fine powders to carry out X-ray powder diffraction (XRD) measurement. Parts of the sintered BSN25 pellets were crushed and ground into fine powders to perform the X-ray fluorescence (XRF) and thermogravimetric (TG) measurements. The atomic ratio of the as-prepared BSN25 powders was determined to be Ba: Sc: Nb = 1.016(16): 0.770(18): 0.244(5) by XRF (NEX DE, Rigaku Co.), which agreed with that of the nominal composition within two times standard deviation. Cu Ka XRD data of the as-prepared BSN25, BSN35, and BSN45 powders were measured at 24 °C by a laboratory-based X-ray diffractometer (MiniFlex, Rigaku Co.). The lattice parameter of the as-prepared BSN25, BSN35, and BSN45 powders was refined by Rietveld analyses of the XRD data using Z-Rietveld<sup>1</sup> software. SEM observation of a sintered pellet of BSN25 was performed using a VE-8800 SEM microscope (Keyence Co.) (Fig. S11).

Wet BSN25 powders for thermogravimetric-mass spectrometric (TG-MS), infrared (IR), and Raman scattering measurements were prepared as follows. The as-prepared BSN25 powders were heated to 1000 °C in dry air (water vapor partial pressure  $P(H_2O) < 1.5 \times 10^{-4}$  atm) and kept for 1 h to remove water, and then the atmosphere was switched to H<sub>2</sub>O-saturated air flow ( $P(H_2O) = 0.02$  atm) at the same temperature 1000 °C. In cooling process, the sample was kept for 1 h at 1000, 900, 800, 700, 600, 500, 400, 300, 200, and 100 °C, and for 4 h at 50 °C to reach equilibrium. TG-MS analyses of the wet BSN25 powders were performed using RIGAKU Thermo Mass Photo under He flow at a heating rate of 20 °C min<sup>-1</sup> up to 800 °C. The proton concentration of BSN25 was investigated from 1000 to 100 °C by TG analysis (STA449 Jupiter, Netzsch Co.; Fig. S10). The as-prepared BSN25 powders were first heated to 1000 °C in dry air ( $P(H_2O) < 1.5 \times 10^{-4}$  atm) and kept for 1 h to dehydrate. The gas subsequently switched to wet air  $(P(H_2O) = 0.02 \text{ atm})$ . In cooling process, the sample weight was recorded keeping the temperature at 1000, 950, 900, 850, 800, 750, 700, 650, 600, 550, 500, 450, 400, 350, 300, 250, 200, 150, 100 and 50 °C for 1 h to reach equilibrium. The proton concentration y in BSN25 was calculated from the weight increase assuming that the sample contains no protons (y = 0) at 1000 °C in dry air and that the weight increase was due to water incorporation only. The hydration enthalpy and entropy were estimated using the TG data (ESI Note no.1, Table S4, and Fig. S12). Raman spectrum of the wet BSN25 powders was collected using NRS-4100 (JASCO Co.) with excitation wavelength of 532 nm. IR data for the wet BSN25 powders were measured using FT/IR-4200 (JASCO Co.).

Impedance spectra of the sintered pellet of BSN25 (5 mm in diameter, 4 mm in thickness), BSN35 (5 mm in diameter, 14 mm in thickness), and BSN45 (5 mm in diameter, 6 mm in thickness) with Pt electrodes were

recorded with a Solartron 1260 impedance analyzer in the frequency range from 0.1 Hz to 10 MHz with an applied alternating voltage of 100 mV in wet air ( $P(H_2O) = 0.02$  atm) and dry air ( $P(H_2O) < 1.5 \times 10^{-4}$  atm) on cooling. Equivalent-circuit analyses were performed to extract the bulk and grain boundary conductivities using *Zview* software (Scribner Associates, Inc.). The Lin-KK software was employed to perform the Kramers–Kronig (KK) transformation on the collected impedance data.<sup>2,3,4</sup> Oxygen partial pressure  $P(O_2)$  dependencies of the DC electrical conductivity of the sintered pellet of BSN25 (5 mm in diameter and 13 mm in length) were investigated by a DC four-probe method with Pt electrodes using a mixture of O<sub>2</sub>, air, N<sub>2</sub> and 5% H<sub>2</sub> in N<sub>2</sub> under wet conditions ( $P(H_2O) = 0.02$  atm) where the  $P(O_2)$  was monitored with an oxygen sensor placed at the outlet of the apparatus. The isotope effect of the sintered pellet of BSN25 was evaluated by the DC electrical conductivity measurements in D<sub>2</sub>O- and H<sub>2</sub>O-saturated air ( $P(D_2O) = P(H_2O) = 0.02$  atm).

Neutron diffraction and total scattering experiments of wet pellets of BSN25 were performed at  $-243 \,^{\circ}$ C with the neutron total scattering spectrometer NOVA at the MLF of the J-PARC.<sup>5</sup> The wet pellets of BSN25 for neutron diffraction measurements were prepared as follows. The sintered pellets of BSN25 were heated to 1000 °C in dry air ( $P(H_2O) < 1.5 \times 10^{-4}$  atm) and kept for 1 h in order to remove water, and then the atmosphere was switched to D<sub>2</sub>O-saturated air flow ( $P(D_2O) = 0.02$  atm) at the same temperature 1000 °C. In cooling process, the sample was kept for 2 h at 1000, 900, 800, 700, 600, 500, 400, 300, 200, 100, and 25 °C to reach equilibrium. Rietveld analyses were performed with *Z-Rietveld*<sup>1</sup> using neutron diffraction data taken with the backscattering bank of the NOVA. The neutron scattering data obtained using the 90 degree bank were transformed into the structure function S(Q) and the atomic pair distribution function G(r) by using the program installed at NOVA.<sup>6</sup> Bond-valence based energy landscape (BVEL) for a test proton in BSN25 was calculated using refined crystal parameters at  $-243 \,^{\circ}C$  with the *SoftBV* program.<sup>78</sup>

Static DFT calculations and *ab initio* molecular dynamics (AIMD) simulations were performed for the  $2 \times 2 \times 2$  supercell Ba<sub>8</sub>Sc<sub>6</sub>Nb<sub>2</sub>O<sub>24</sub>H<sub>4</sub> (= [BaSc<sub>0.75</sub>Nb<sub>0.25</sub>O<sub>3</sub>H<sub>0.5</sub>]<sub>8</sub>) using the Vienna ab initio simulation package (VASP)<sup>9</sup> code with the projector augmented wave (PAW) method and the Perdew–Burke–Ernzerhof (PBE) functional in the generalized gradient approximation (GGA). The cut-off energy was set to 400 eV for all calculations. A  $3\times3\times3$  set of *k*-point meshes was used in Monkhorst-Pack scheme. Lattice parameters and atomic coordinates of all the three models with different Nb and Sc atomic configurations of Ba<sub>8</sub>Sc<sub>6</sub>Nb<sub>2</sub>O<sub>24</sub>H (= [BaSc<sub>0.75</sub>Nb<sub>0.25</sub>O<sub>3</sub>]<sub>8</sub>) were optimized in the space group *P*1 using the background charge. Based on the model having the minimum energy among the three models, the hydrogen atoms were put near selected oxygen atoms and the OH distance was set to about 1 Å in the initial structure of Ba<sub>8</sub>Sc<sub>6</sub>Nb<sub>2</sub>O<sub>24</sub>H<sub>4</sub>. Lattice parameters and atomic coordinates of Ba<sub>8</sub>Sc<sub>6</sub>Nb<sub>2</sub>O<sub>24</sub>H<sub>4</sub>, which was used as the initial structure of the AIMD simulations. The AIMD simulations were performed at a constant temperature 1500 °C with a time step of 1 fs within the canonical ensemble (NVT) using a Nosé thermostat, after the heating process (1 °C fs<sup>-1</sup>) within the microcanonical (NVE) ensemble. The refined crystal structure, bond valence based energy landscape and the probability density distribution of H atoms from the AIMD simulations were drawn with *VESTA* 3.<sup>10</sup>



**Figure S1.** Cu K $\alpha$  X-ray powder diffraction pattern of as-prepared (a) BaSc<sub>0.55</sub>Nb<sub>0.45</sub>O<sub>2.95-y/2</sub>(OH)<sub>y</sub> (x = 0.45; BSN45), (b) BaSc<sub>0.65</sub>Nb<sub>0.35</sub>O<sub>2.85-y/2</sub>(OH)<sub>y</sub> (x = 0.35; BSN35), (c) BaSc<sub>0.75</sub>Nb<sub>0.25</sub>O<sub>2.75-y/2</sub>(OH)<sub>y</sub> (x = 0.25; BSN25), and (d) BaSc<sub>0.8</sub>Nb<sub>0.2</sub>O<sub>2.7-y/2</sub>(OH)<sub>y</sub> (x = 0.20; BSN20) powders at 24 °C. *hkl* denotes the reflection index of the primitive cubic cell. Asterisk denotes the impurity phase Ba<sub>3</sub>Sc<sub>4</sub>O<sub>9</sub>. (e) Lattice parameter of as-prepared BaSc<sub>1-x</sub>Nb<sub>x</sub>O<sub>2.5+(2x-y)/2</sub>(OH)<sub>y</sub> versus *x* at 24 °C. Error bars represent the standard deviations. The lattice parameter of BaSc<sub>1-x</sub>Nb<sub>x</sub>O<sub>2.5+(2x-y)/2</sub>(OH)<sub>y</sub> decreases with an increase of Nb content *x*, indicating the formation of solid solutions of BaSc<sub>1-x</sub>Nb<sub>x</sub>O<sub>2.5+(2x-y)/2</sub>(OH)<sub>y</sub>. The refined lattice parameters at 24 °C of BSN20, BSN25, BSN35, and BSN45 were 4.1445(6), 4.1454(6), 4.1378(5), and 4.1255(7) Å, respectively.



**Figure S2**. Equivalent circuits used to model the impedance spectra of BSN25 at (a) 46 °C, (b) 90 °C, (c) 145 °C, and (d) 193–390 °C. *R*, *C*, CPE, and W<sub>o</sub> denote a resistance, capacitance, constant phase element, and open Warburg element, respectively. The subscripts "bulk", "gb", and "ele" denote the bulk, grain boundary, and electrode, respectively.



**Figure S3**. Complex impedance plots of BSN25 at (a) 46, (b) 193, (c) 287 and (d) 390 °C in wet air. Each number denotes the frequency at a blue closed circle. The red solid line represents the fitting curve. The green dotted, high-frequency semicircle represents the bulk response.  $R_b$  denotes the bulk resistance.



**Figure S4**. Residual plots of (a) the measured impedance data obtained by the Kramers-Kronig transformation and (b) the equivalent circuit fitting of BSN25 in wet air at 193 °C.

Table S1.	Capacitances	for bulk $C_{\rm b}$	and grain	boundary (	$C_{\rm gb}$ of	f BSN25 in v	vet air.
-----------	--------------	----------------------	-----------	------------	-----------------	--------------	----------

<i>T</i> (°C)	С <sub>ь</sub> (F)	$C_{ m gb}$ (F)
46	1.01×10 <sup>-11</sup>	6.73×10 <sup>-10</sup>
90	9.47×10 <sup>-12</sup>	7.41×10 <sup>-10</sup>
145		9.56×10 <sup>-10</sup>
193		4.81×10 <sup>-10</sup>
235		3.83×10 <sup>-10</sup>
287		2.14×10 <sup>-10</sup>
337		3.18×10 <sup>−9</sup>
390		1.37×10 <sup>−9</sup>



Figure S5. Arrhenius plots of bulk (red circles) and grain-boundary (blue circles) conductivities of BSN25 in wet air.



**Figure S6**. Arrhenius plots of bulk conductivity of BSN25 (red circles and line), BSN35 (green circles and line), and BSN45 (blue circles and line) in wet air.



**Figure S7**. (a) H/D isotope effect on the DC electrical conductivity  $\sigma_{DC}$  of BSN25. (b) Oxygen partial pressure  $P(O_2)$  dependencies of the  $\sigma_{DC}$  for BSN25 at 300 °C (red closed circles and solid line) and 100 °C (blue closed circles and solid line) under wet conditions.



**Figure S8**. (a) Arrhenius plots of bulk conductivity of BSN25 in wet air ( $\sigma_{wet}$ , blue open circles) and dry air ( $\sigma_{dry}$ , black open circles and line). Arrhenius plots of the bulk proton conductivity of BSW (red closed circles and line). Here, the bulk proton conductivity  $\sigma_{H^+}$  was estimated using the equation,  $\sigma_{H^+} = \sigma_{wet} - \sigma_{dry}$ . (b) Temperature dependence of apparent proton transport number in BSN25. The apparent proton transport number was calculated by the equation,  $t_{H^+} = \sigma_{H^+}/\sigma_{wet}$ .



**Figure S9**. Cu K $\alpha$  X-ray powder diffraction patterns of BSN25 after annealing at room temperature for 24 h under (a) wet CO<sub>2</sub> (*P*(H<sub>2</sub>O) = 0.02 atm) and (b) before annealing.



Figure S10. Water uptake of as-prepared BSN25 in wet air.

	<b>Base</b> 0.731	100.23 0 2.9982(12	(2) = 0.490(2)	10 01				
Site, atom la	bel X atom Y	g <sup>a</sup>	Wyckoff position	x	у	Z	$U_{\rm iso}$ (Å <sup>2</sup> ) <sup>b</sup>	BVS <sup>c</sup>
Ba	Ba	1 <i>d</i>	1 <i>b</i>	1/2	1/2	1/2	0.01771(4)	2.0
Sc/Nb	Sc	$0.75^{d}$	1 <i>a</i>	0	0	0	0.01839(3)	3.2
Sc/Nb	Nb	$0.25^{d}$	1 <i>a</i>	0	0	0	0.01839(3)	
0	0	0.9995(4)	3 <i>d</i>	1/2	0	0	0.01532(3)	2.1
D	D	0.02069(10)	24 <i>m</i>	0.4301(3)	0.2297(4)	0	0.0193(3)	0.8

**Table S2.** Results of the refined crystal parameters and reliability factors in Rietveld analysis of the neutron diffraction data of  $BaSc_{0.75}Nb_{0.25}O_3D_{0.5} \approx BaSc_{0.75}Nb_{0.25}O_{2.501(12)}(OD)_{0.496(2)}$  (=  $BSN25 = BaSc_{0.75}Nb_{0.25}O_{2.75}$ ) 0.2482(12)  $D_2O = BaSc_{0.75}Nb_{0.25}O_{2.9982(12)}D_{0.496(2)}$ ) at -243 °C.

Crystal system: cubic, Space group:  $Pm^3m$ ,  $R_{wp} = 6.15\%$ ,  $R_B = 2.79\%$ ,  $R_F = 4.67\%$ , Lattice parameter: a = 4.165220(3) Å.

<sup>*a*</sup> Occupancy factor of *Y* atom at the *X* site. *x*, *y*, and *z*: atomic coordinates.

<sup>*b*</sup>  $U_{iso} = U_{iso}(Y; X)$ : Isotropic atomic displacement parameter of *Y* atom at the *X* site. Linear constraints in the Rietveld analysis:  $U_{iso}(Sc; Sc/Nb) = U_{iso}(Nb; Sc/Nb)$ .

<sup>*c*</sup> BVS: Bond valence sum. Here, the bond-valence parameters (Ref. <sup>11</sup>) were used for the calculation of BVSs for Ba, O, and Sc/Nb. The bond-valence parameter of D atom in Ref. <sup>12</sup> was used for the calculation of BVS.

<sup>*d*</sup> Since the refined occupancy factors of Ba, Sc and Nb atoms agreed with 1, 0.75 and 0.25, respectively, within three estimated standard deviations in preliminary analyses, respectively, they were fixed to these values.

**Table S3.** Atomic coordinates of hydrogen atom of wet BSN25 and  $BaSc_{0.8}Mo_{0.2}O_{2.8-y/2}(OD)_y$  (Ref. <sup>13</sup>), which were refined by Rietveld analysis of neutron diffraction data. Average atomic coordinates of proton of  $Ba_8Sc_6Nb_2O_{20}(OH)_4$ , which were optimized by DFT calculations.

Composition	Atomic coordinates of hydrogen atom					
	x	у	z			
BaSc <sub>0.75</sub> Nb <sub>0.25</sub> O <sub>2.501(12)</sub> (OD) <sub>0.496(2)</sub>	0.4301(3)	0.2297(4)	0			
Ba <sub>8</sub> Sc <sub>6</sub> Nb <sub>2</sub> O <sub>20</sub> (OH) <sub>4</sub>	0.411(18)	0.233(12)	0.002(6)			
BaSc <sub>0.8</sub> Mo <sub>0.2</sub> O <sub>2.6400(15)</sub> (OD) <sub>0.3173(17)</sub>	0.4254(10)	0.2307(15)	0			



Figure S11. SEM micrograph of a sintered pellet of BaSc<sub>0.75</sub>Nb<sub>0.25</sub>O<sub>2.75-y/2</sub>(OH)<sub>y</sub> (BSN25). The sample was

thermally etched at 1570 °C for 1 h prior to the SEM observation. The average grain size was estimated to be 3  $\mu$ m in diameter.

#### ESI Note no.1

Thermodynamic parameters for the hydration of BSN25 (x = 0.25 in BaSc<sub>1-x</sub>Nb<sub>x</sub>O<sub>2.5+x-y/2</sub>(OH)<sub>y</sub> $v_{0.5-x-y/2}$ ) was obtained using active and inactive oxygen vacancies.<sup>13</sup> The hydration for the active oxygen vacancies can be expressed by the following equation.

$$H_{2}O + v(1)_{5}^{\frac{5}{3}} + O_{5}^{\frac{1}{3}} \approx 2(OH)_{5}^{\frac{2}{3}}$$

$$v(1)_{5}^{\frac{5}{3}} + O_{5}^{\frac{1}{3}} \approx 2(OH)_{5}^{\frac{2}{3}} = 0$$
Eq. (S2)

Here, the  $\overline{6}^0$  is the active oxygen vacancy at the anion  $6^\circ$  site. Thus, the equilibrium constants  $K_w$  for the hydration [Eq. (S1)] can be expressed as:

$$K_{w} = \frac{\left[(0H)_{5}^{\frac{2}{3}}\right]^{2}}{\left[v(1)_{5}^{\frac{5}{3}}\right]\left[0, \frac{1}{3}\right]}P(H_{2}0)}$$
Eq. (S3)

Here,  $P(H_2O)$  is water vapor partial pressure. The total concentration of the active and inactive oxygen  $\frac{5}{2}$ .

$$\begin{bmatrix} v_{5}^{3} \\ \overline{6}^{0} \\ is \\ \begin{bmatrix} v_{5}^{3} \\ \overline{6}^{0} \end{bmatrix} = \begin{bmatrix} v(1)_{5}^{3} \\ \overline{6}^{0} \end{bmatrix} + \begin{bmatrix} v(2)_{5}^{3} \\ \overline{6}^{0} \end{bmatrix}$$
Eq. (S4)  
$$\begin{bmatrix} v(2)_{5}^{3} \\ \overline{5}^{0} \end{bmatrix}$$

Here,  $\overline{6}^{\circ}$  is the concentration of the inactive oxygen vacancies. The sum of numbers of oxygen vacancies, oxide ions and hydroxide ions in BaSc<sub>1-x</sub>Nb<sub>x</sub>O<sub>2.5+x-y/2</sub>(OH)<sub>y</sub> $v_{0.5-x-y/2}$  equals to 3:

$$\begin{bmatrix} v_{5}^{\frac{5}{3}} \\ e_{5}^{\frac{7}{3}} \end{bmatrix} + \begin{bmatrix} 0_{5}^{\frac{1}{3}} \\ e_{5}^{\frac{7}{3}} \end{bmatrix} + \begin{bmatrix} (0H)_{5}^{\frac{2}{3}} \\ e_{6}^{\frac{7}{3}} \end{bmatrix} = 3$$
Eq. (S5)

Electroneutrality condition in  $BaSc_{1-x}Nb_xO_{2.5+x-y/2}(OH)_y v_{0.5-x-y/2}$  can be expressed as follows assuming negligible hole concentration.

$$2\left[Nb_{Sc}^{\bullet\bullet}\right] + \frac{5}{3}\left[v_{\frac{5}{6}0}^{\frac{5}{3}\bullet}\right] + \frac{2}{3}\left[(OH)_{\frac{5}{6}0}^{\frac{2}{3}\bullet}\right] = \frac{1}{3}\left[O_{\frac{5}{6}0}^{\frac{1}{3}}\right]$$
Eq. (S6)

Substituting Eq. (S4) into Eq. (S5) yields

$$[v_{\frac{5}{6}0}^{\frac{5}{3}\bullet}] = \frac{1}{2}(1 - [(OH)_{\frac{5}{6}0}^{\frac{2}{3}\bullet}] - 2[Nb_{Sc}^{\bullet\bullet}])$$
Eq. (S7)

Substituting Eq. (S4), Eq. (S5) and Eq. (S6) into Eq. (S3) yields

$$K_{w} = \frac{4[(OH)_{5}^{\frac{2}{3}}]^{2}}{(5 - [(OH)_{5}^{\frac{2}{3}}] + 3[Mo_{5c}^{\bullet\bullet\bullet}])(1 - [(OH)_{5}^{\frac{2}{3}}] - 2[Nb_{5c}^{\bullet\bullet}] - 2[v(2)_{5}^{\frac{5}{3}}])P(H_{2}O)}$$
  
Eq. (S8)  
The concentration of inactive oxygen vacancy  

$$[v(2)_{5}^{\frac{5}{3}}]$$
 was calculated by the following equation,  

$$[v(2)_{5}^{\frac{5}{3}}]$$

$$[\nu(2)_{5}^{\frac{1}{3}\bullet}] = \frac{1}{2}(1 - 2[Nb_{Sc}^{\bullet\bullet}] - C_{H,Max})$$

Eq. (S9)

Here,  $C_{H,Max}$  is the measured maximum of proton concentration (i.e., proton concentration at 100 °C). The equilibrium constants  $K_w$  for van 't Hoff plots were calculated by Eq. (S7). The hydration enthalpy  $\Delta H^{\circ}$  and hydration entropy  $\Delta S^{\circ}$  were estimated by Eq. (S9) and van 't Hoff plots (**Table S4, Fig. S12**).

$$K_w = \exp\left(-\frac{\Delta H}{RT}\right) \exp\left(\frac{\Delta S}{R}\right)$$
 Eq. (S10)

Here, R represents the gas constant.

p. 13



Figure S12. van 't Hoff plot of the equilibrium constant  $K_w$  for the hydration of BSN25. The  $K_w$  was calculated using Eq. (S8) in ESI Note no. 1.

**Table S4.** Hydration enthalpy and entropy of BSN25,  $BaZr_{0.9}Y_{0.1}O_{2.95-y/2}(OH)_y$  (Ref. <sup>14</sup>), and  $BaZr_{0.85}Y_{0.15}O_{2.925-y/2}(OH)_y$  (Ref. <sup>14</sup>) at 500–1000, 500–900, and 500–900 °C, respectively. The hydration enthalpy and entropy of BSN25 were estimated using the van 't Hoff plots (**Fig. S12**).

Composition	<i>ΔH</i> ° (kJ mol⁻¹)	ΔS° (J K⁻¹ mol⁻¹)
BaSc <sub>0.75</sub> Nb <sub>0.25</sub> O <sub>2.75-y/2</sub> (OH) <sub>y</sub>	-86(4)	-82(4)
BaZr <sub>0.9</sub> Y <sub>0.1</sub> O <sub>2.95-y/2</sub> (OH) <sub>y</sub>	-80	-89
BaZr <sub>0.85</sub> Y <sub>0.15</sub> O <sub>2.925-y/2</sub> (OH) <sub>y</sub>	-83	-92

The hydration enthalpy and entropy of BSN25 have similar values with those of proton conducting perovskites  $BaZr_{0.9}Y_{0.1}O_{2.95-y/2}(OH)_y$  and  $BaZr_{0.85}Y_{0.15}O_{2.925-y/2}(OH)_y$ .



Figure S13. Optimized structure of Ba<sub>8</sub>Sc<sub>6</sub>Nb<sub>2</sub>O<sub>24</sub>H<sub>4</sub>, which was obtained by static DFT calculations.



**Figure S14**. Pair distribution function (PDF) data of hydrated (deuterated) BSN25 at -243 °C. The PDF was obtained from neutron scattering data taken at -243 °C with NOVA.<sup>5</sup>

### References

- 1 R. Oishi, M. Yonemura, Y. Nishimaki, S. Torii, A. Hoshikawa, T. Ishigaki, T. Morishima, K. Mori and T. Kamiyama, Rietveld analysis software for J-PARC, *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.*, 2009, **600**, 94–96.
- 2 R. A. Vargas-Hernández, Bayesian optimization for calibrating and selecting hybrid-density functional models, *J. Phys. Chem. A*, 2020, **124**, 4053–4061.
- 3 M. Schönleber, D. Klotz and E. Ivers-Tiffée, A method for improving the robustness of linear Kramers-Kronig validity tests, *Electrochim. Acta*, 2014, **131**, 20–27.
- 4 M. Schönleber and E. Ivers-Tiffée, Approximability of impedance spectra by RC elements and implications for impedance analysis, *Electrochem. commun.*, 2015, **58**, 15–19.
- 5 K. Nakajima, Y. Kawakita, S. Itoh, J. Abe, K. Aizawa, H. Aoki, H. Endo, M. Fujita, K. Funakoshi, W. Gong, M. Harada, S. Harjo, T. Hattori, M. Hino, T. Honda, A. Hoshikawa, K. Ikeda, T. Ino, T. Ishigaki, Y. Ishikawa, H. Iwase, T. K. Id, R. K. Id, T. Kawasaki, A. Kimura, R. Kiyanagi, K. Kojima and K. Kusaka, Materials and life science experimental facility (MLF) at the Japan Proton Accelerator Research Complex II : neutron scattering instruments, *Quantum Beam Sci.*, 2017, **1**, 9.
- 6 K. Kodama, N. Igawa, S. Shamoto, K. Ikeda, H. Ohshita, N. Kaneko, T. Otomo, K. Suzuya, A. Hoshikawa and T. Ishigaki, Local structural analysis by using atomic pair distribution function on mixed valence compound LiMn<sub>2</sub>O<sub>4</sub>, *Proceedings of the International Conference on Strongly Correlated Electron Systems (SCES2013)*, 2014, **3**, 013012.
- H. Chen, L. L. Wong and S. Adams, *SoftBV* a software tool for screening the materials genome of inorganic fast ion conductors research papers, *Acta Cryst. B Struct. Sci. Cryst. Eng. Mater.*, 2019, 75, 18–33.
- L. L. Wong, K. C. Phuah, R. Dai, H. Chen, W. S. Chew and S. Adams, Bond Valence Pathway Analyzer—an automatic rapid screening tool for fast ion conductors within softBV, *Chem. Mater.*, 2021, **33**, 625–641.
- 9 G. Kresse and D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B*, 1999, **59**, 1758–1775.
- 10 K. Momma and F. Izumi, *VESTA 3* for three-dimensional visualization of crystal, volumetric and morphology data, *J. Appl. Crystallogr.*, 2011, **44**, 1272–1276.
- 11 I. D. Brown and D. Aitermatt, Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1985, **B41**, 244–247.
- 12 I. D. Brown, *The Chemical Bond in Inorganic Chemistry*, Oxford University Press, Oxford, 2002.
- 13 K. Saito and M. Yashima, High proton conductivity within the 'Norby gap' by stabilizing a perovskite with disordered intrinsic oxygen vacancies, *Nat. Commun.*, 2023, **14**, 7466.
- 14 K. D. Kreuer, S. Adams, W. Münch, A. Fuchs, U. Klock and J. Maier, Proton conducting alkaline earth zirconates and titanates for high drain electrochemical applications, *Solid State Ionics*, 2001, **145**, 295.