

Dopant-Induced Changes of Local Structure for Adjusting the Hydration Ability of Proton-Conducting Lanthanum Scandates

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Partial Conductivities

The total conductivity of $\text{La}_{0.95}\text{M}_{0.05}\text{ScO}_{3-\delta}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) as a function of $p\text{O}_2$ in a dry ($p\text{H}_2\text{O} = 0.1 \text{ kPa}$) and wet ($p\text{H}_2\text{O} = 2.8 \text{ kPa}$) atmosphere was measured by the 4-probe DC method and is shown in Fig. S1. Under air conditions, the conductivity contains three contributions:

$$\sigma_t = \sigma_H + \sigma_O + \sigma_h, \quad (1)$$

where σ_H , σ_O and σ_h are the proton, oxygen-ion and hole conductivities, respectively.

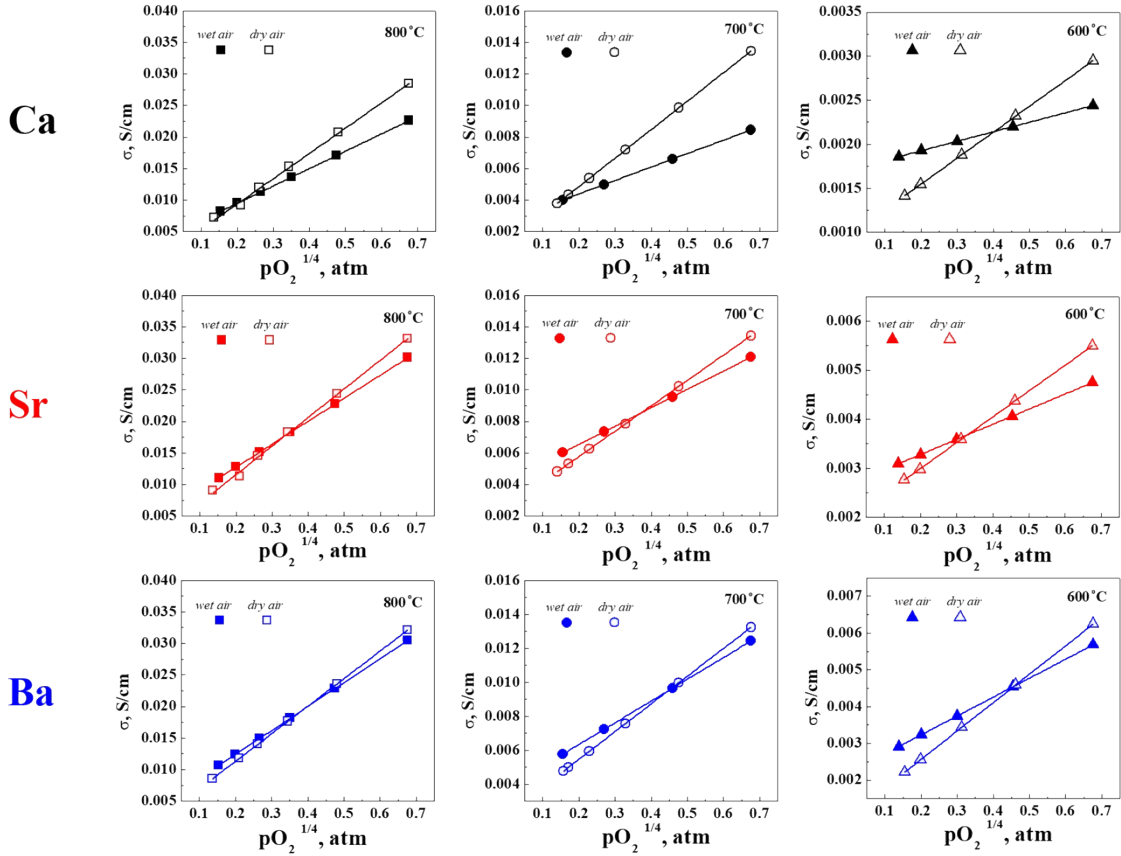


Fig. S1 Total conductivity vs. $p\text{O}_2^{1/4}$ dependencies for $\text{La}_{0.95}\text{M}_{0.05}\text{ScO}_{3-\delta}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$)

Frade¹ and Baek² proposed an approach for calculating partial conductivities based on slope analysis of $\sigma = f(p\text{O}_2)$ dependencies. This approach implies the independence of the mobility of charge carriers on the concentration of components of the gas phase. The following relations are obtained for partial conductivities:

$$\sigma_H = \sigma_H^* \left(\left(1 + \frac{\alpha}{p\text{H}_2\text{O}} \right)^{1/2} - 1 \right) \frac{p\text{H}_2\text{O}}{[(1 + \alpha)^{1/2} - 1]}, \quad (2)$$

$$\sigma_O = \sigma_O^* \left(\left(1 + \frac{\alpha}{p\text{H}_2\text{O}} \right)^{1/2} - 1 \right)^2 \frac{p\text{H}_2\text{O}}{\alpha}, \quad (3)$$

$$\sigma_h = \sigma_h^* \left(\left(1 + \frac{\alpha}{pH_2O} \right)^{1/2} - 1 \right) \left(\frac{pH_2O}{\alpha} \right)^{1/2} pO_2^{1/4}, \quad (4)$$

where σ_H^* is protonic conductivity at $pH_2O = 1$ atm, σ_O^* is oxygen-ion conductivity at $pH_2O = 0$ atm and σ_h^* is hole conductivity at $pO_2 = 1$ atm and $pH_2O = 0$ atm. The value of α is equal to:

$$\alpha = \frac{8x_{eff}}{K_H}, \quad (5)$$

where x_{eff} is the saturation limit for hydration or effective concentration of the dopant in the positions of La and K_H is the equilibrium constants of hydration.

Based on equation (7), we can find σ_h as the slope of the experimental dependence $\sigma_t = f(pO_2)^{1/4}$. The α value can be calculated by combining two equations (4) for two humidity values and obtaining the following equation:

$$\frac{\sigma_h^{(1)}}{\sigma_h^{(2)}} = \frac{\sigma_h^* \left(\left(1 + \frac{\alpha}{pH_2O^{(1)}} \right)^{1/2} - 1 \right) \left(\frac{pH_2O^{(1)}}{\alpha} \right)^{1/2}}{\sigma_h^* \left(\left(1 + \frac{\alpha}{pH_2O^{(2)}} \right)^{1/2} - 1 \right) \left(\frac{pH_2O^{(2)}}{\alpha} \right)^{1/2}} = \frac{\left(1 + \frac{pH_2O^{(1)}}{\alpha} \right)^{1/2} - \left(\frac{pH_2O^{(1)}}{\alpha} \right)^{1/2}}{\left(1 + \frac{pH_2O^{(2)}}{\alpha} \right)^{1/2} - \left(\frac{pH_2O^{(2)}}{\alpha} \right)^{1/2}}. \quad (6)$$

The resulting α values at different temperatures are shown in Table S1.

Table S1 The values of α calculated for $La_{0.95}M_{0.05}ScO_{3-\delta}$ (M = Ca, Sr, Ba) at different temperatures

T, °C	α , atm		
	$La_{0.95}Ca_{0.05}ScO_{3-\delta}$	$La_{0.95}Sr_{0.05}ScO_{3-\delta}$	$La_{0.95}Ba_{0.05}ScO_{3-\delta}$
800	0.1286	0.4258	0.8934
700	0.0200	0.1605	0.3022
600	0.0091	0.0540	0.1011

Next, we can find σ_H and σ_O from the value of the total ionic conductivity (σ_i , the intercept with the vertical axis of $\sigma_t = f(pO_2)^{1/4}$ experimental dependency) by combining equations (2) and (3) for two humidity values:

$$\frac{\sigma_i^{(1)}}{\sigma_i^{(2)}} = \frac{\sigma_H^{(1)} + \sigma_O^{(1)}}{\sigma_H^{(2)} + \sigma_O^{(2)}} = \frac{\sigma_H^* \left(\left(1 + \frac{\alpha}{pH_2O^{(1)}} \right)^{1/2} - 1 \right) \left(\frac{pH_2O^{(1)}}{[(1+\alpha)^{1/2} - 1]} \right)^{1/2} + \sigma_O^* \left(\left(1 + \frac{\alpha}{pH_2O^{(1)}} \right)^{1/2} - 1 \right) \frac{pH_2O^{(1)}}{\alpha}}{\sigma_H^* \left(\left(1 + \frac{\alpha}{pH_2O^{(2)}} \right)^{1/2} - 1 \right) \left(\frac{pH_2O^{(2)}}{[(1+\alpha)^{1/2} - 1]} \right)^{1/2} + \sigma_O^* \left(\left(1 + \frac{\alpha}{pH_2O^{(2)}} \right)^{1/2} - 1 \right) \frac{pH_2O^{(2)}}{\alpha}}. \quad (7)$$

XRD and PDF

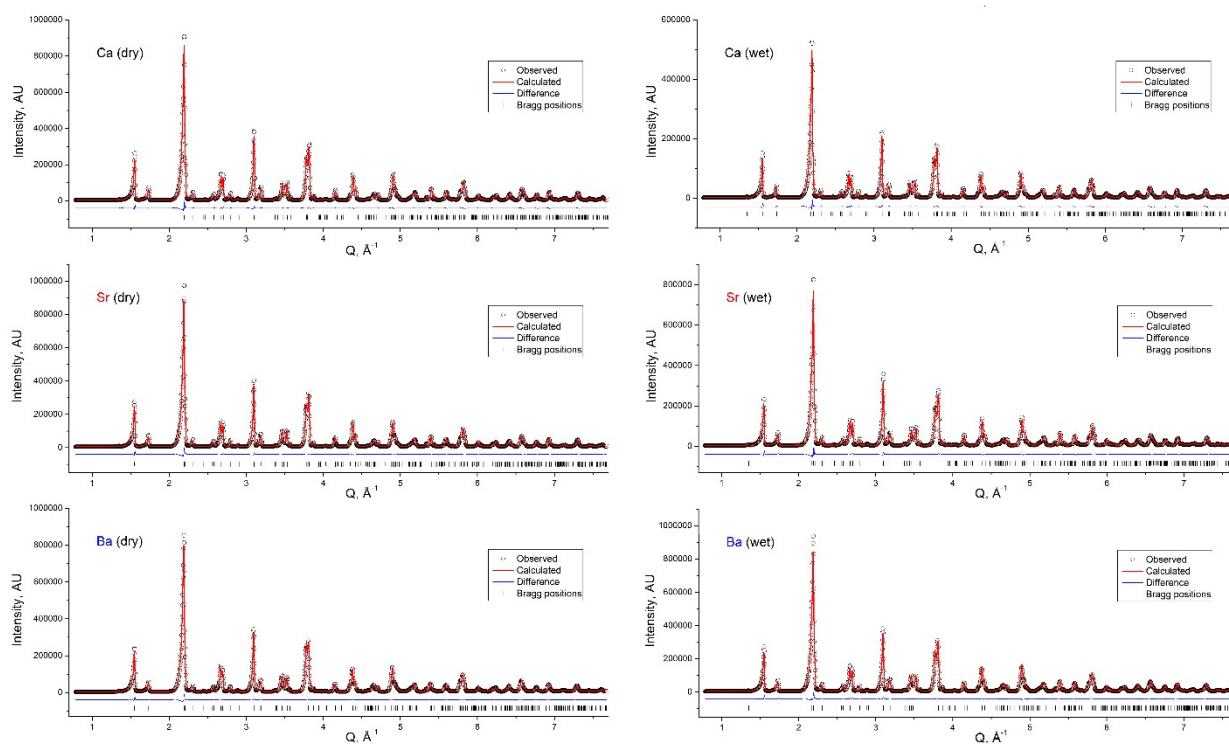


Fig. S2 XRD patterns with Rietveld refinements for $\text{La}_{0.95}\text{M}_{0.05}\text{ScO}_{3-\delta}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) samples in dry and saturated with water (wet) states

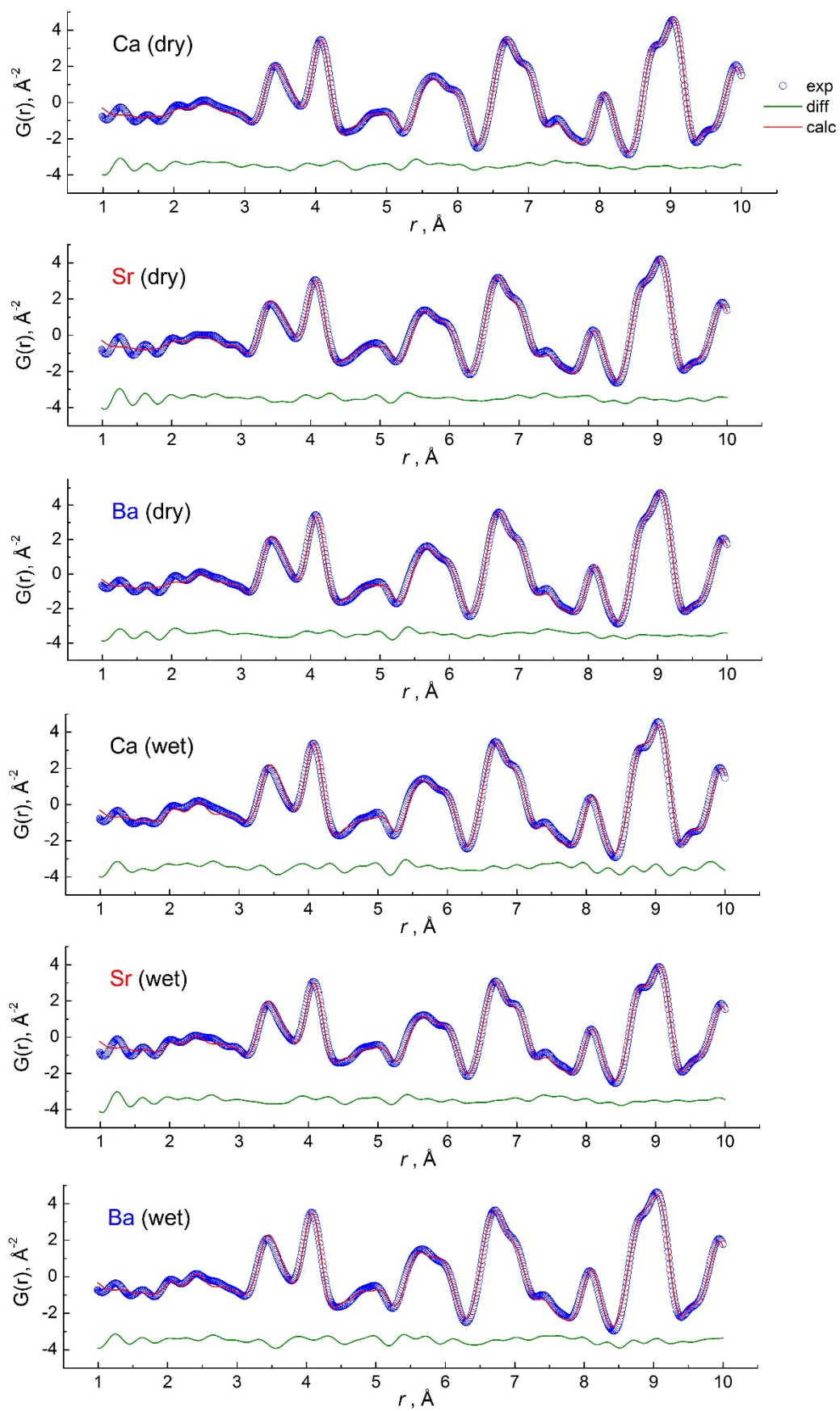


Fig. S3 Refined local structure using X-ray PDF for $\text{La}_{0.95}\text{M}_{0.05}\text{ScO}_{3-\delta}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) samples in dry and saturated with water (wet) states

Interatomic distances were calculated for the indicated atoms (according to the type of atom) up to 10 Å. There are 4 A-type positions, 4 B-type positions, 8 O1-type positions and 4 O2-type positions in the original unit cell. Atoms are numbered in the following order: La 1-4, Sc 5-8, O1 9-16 and O2 17-20. Table S2 presents the interatomic distances for the first coordination spheres of atoms, which corresponds to the lengths of chemical bonds.

Table S2 Bond length according to PDF

Pairs	Bond length, Å		
	Ca	Sr	Ba
<i>La-O</i>			
La(1)-O(18), La(2)-O(17), La(3)-O(20), La(4)-O(19)	2.3347	2.3238	2.4613
La(1)-O(13), La(1)-O(15), La(2)-O(14), La(2)-O(16), La(3)-O(9), La(3)-O(11), La(4)-O(10), La(4)-O(12)	2.4422	2.4118	2.4315
La(1)-O(19), La(2)-O(20), La(3)-O(17), La(4)-O(18)	2.4679	2.5087	2.4319
La(1)-O(10), La(1)-O(2), La(2)-O(9), La(2)-O(11), La(3)-O(14), La(3)-O(16), La(4)-O(13), La(4)-O(15)	2.6957	2.7185	2.7326
La(1)-O(9), La(1)-O(11), La(2)-O(10), La(2)-O(12), La(3)-O(13), La(3)-O(15), La(4)-O(14), La(4)-O(16)	2.9115	2.9048	2.8935
La(1)-O(19), La(2)-O(20), La(3)-O(17), La(4)-O(18)	3.3646	3.3324	3.3684
La(1)-O(14), La(1)-O(16), La(2)-O(13), La(2)-O(15), La(3)-O(10), La(3)-O(12), La(4)-O(9), La(4)-O(11)	3.5562	3.5829	3.5601
La(1)-O(18), La(2)-O(17), La(3)-O(20), La(4)-O(19)	3.5816	3.5798	3.4605
<i>Sc-O</i>			
Sc(5)-O(9), Sc(5)-O(13), Sc(6)-O(10), Sc(6)-O(14), Sc(7)-O(11), Sc(7)-O(15), Sc(8)-O(12), Sc(8)-O(16)	1.9605	1.977	1.9890
Sc(5)-O(17), Sc(5)-O(19), Sc(6)-O(18), Sc(6)-O(20), Sc(11)-O(17), Sc(11)-O(19), Sc(12)-O(18), Sc(12)-O(20)	2.1238	2.1178	2.1120
Sc(5)-O(12), Sc(5)-O(16), Sc(6)-O(11), Sc(6)-O(15), Sc(7)-O(10), Sc(7)-O(14), Sc(8)-O(9), Sc(8)-O(13)	2.2401	2.2396	2.2209

References

- 1 J. R. Frade *Solid State Ionics*, 1995, **78**, 87–97. [DOI: 10.1016/0167-2738(95)00008-T]
- 2 H. D. Baek *Solid State Ionics*, 1998, **110**, 255–262. [DOI: 10.1016/S0167-2738(98)00138-6]