

Supporting Information

"Free" Volume Expansion and Formation Enthalpy of Defects as Key Parameters Tuning the Oxide Ionic Conductivity in Derivatives of β -La₂Mo₂O₉

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1. Thermal evolution of O1-cation bond lengths, of the distance between O1 and the $[(La/Ba)_3]$ base and of bond angles within the $[O1(La/Ba)_3Mo]$ anti-tetrahedral basic unit as a function of temperature in $\beta-La_{1.85}Ba_{0.15}Mo_2O_{8.925}$.

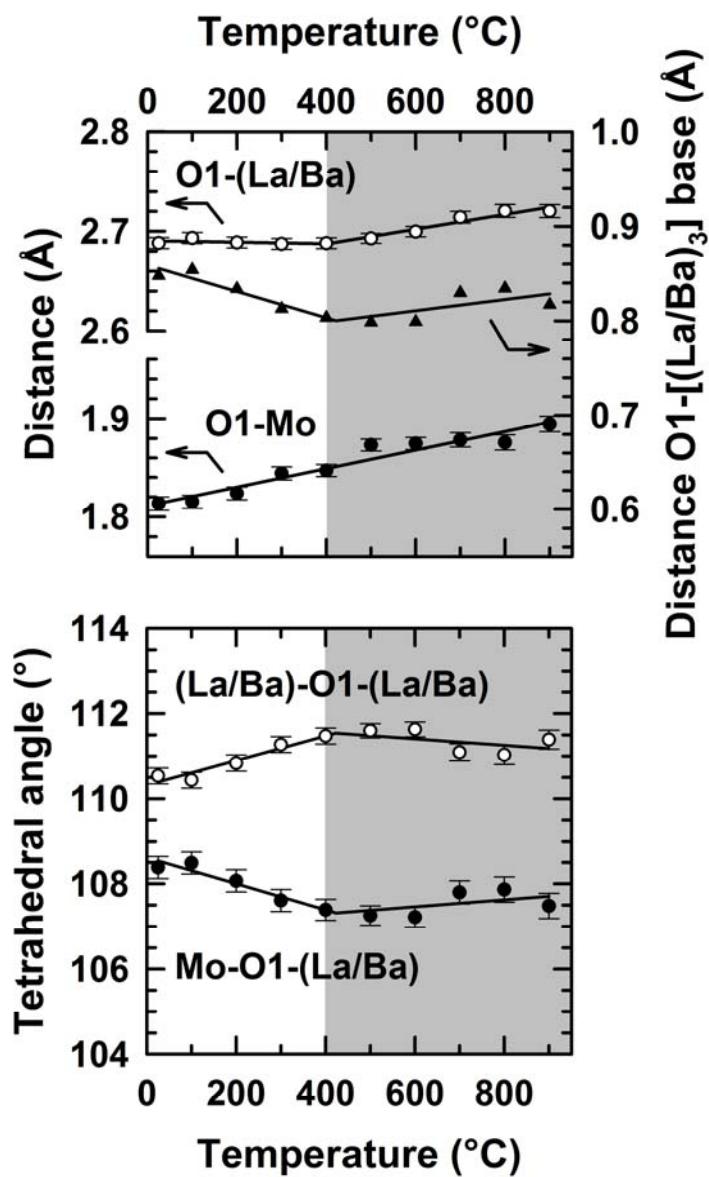


Figure S1

2. Dependence of the electrical conductivity at high temperature fitted with the Vogel-Tammann-Fulcher (VTF) model.

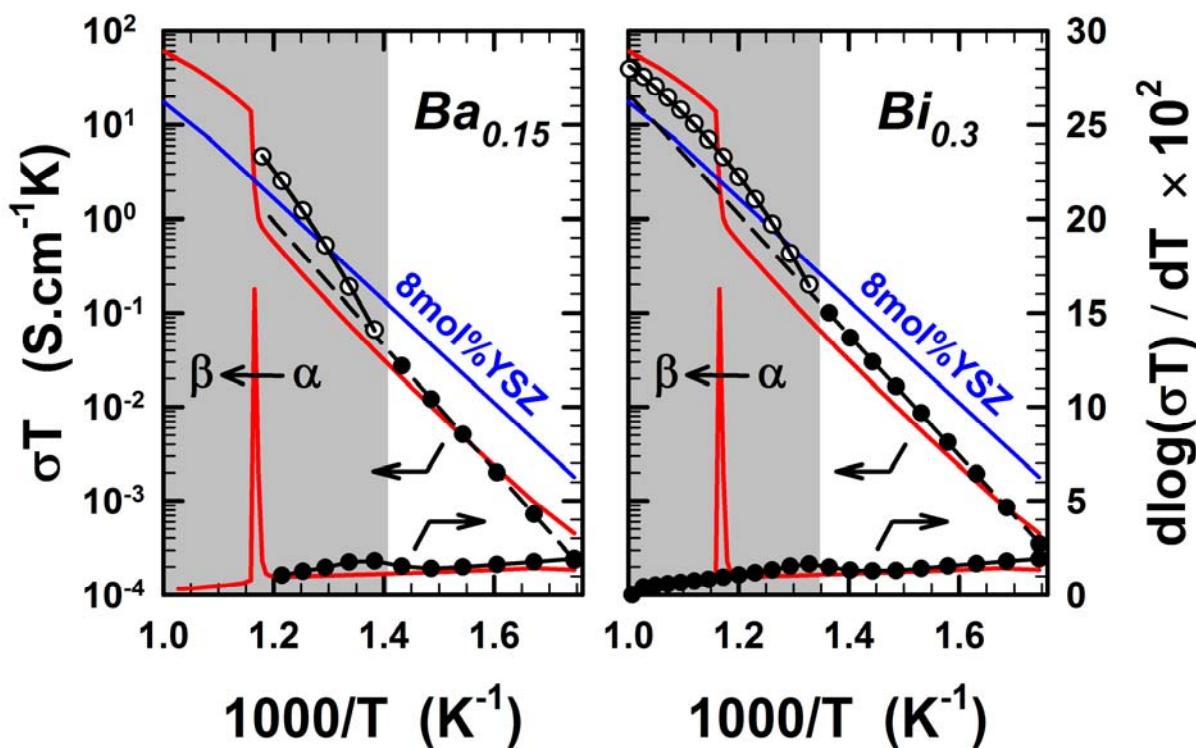


Figure S2 : Temperature dependence of the electrical conductivity of $\beta-\text{La}_{1.7}\text{Bi}_{0.3}\text{Mo}_2\text{O}_9$ (black and open circles) and of $\beta-\text{La}_{1.85}\text{Ba}_{0.15}\text{Mo}_2\text{O}_{8.925}$ (black and open circles) compared to that of $\text{La}_2\text{Mo}_2\text{O}_9$ (pellet sintered 3h at 1000°C, relative density 96(1)% of theoretical density, solid red line) and to that of 8mol% yttria stabilized zirconia (solid blue line, from reference ³). The conductivity plot was fitted with a conventional Arrhenius law in the linear part at low temperature (dashed black line) and with the empirical VTF model when departure from linearity is observed at higher temperature (solid black line). At the bottom, plot of the first derivative of the conduction with respect to temperature is shown (black circles).

Table S1 : Sintering conditions, relative density and parameters of the Arrhenius and the Vogel-Tammann-Fulcher (VTF) –type laws determined for $\beta-\text{La}_{1.7}\text{Bi}_{0.3}\text{Mo}_2\text{O}_9$ and $\beta-\text{La}_{1.85}\text{Ba}_{0.15}\text{Mo}_2\text{O}_{8.925}$

Composition	Sintering Conditions	Relative density (%)	Arrhenius regime $\sigma T = \sigma_0 \exp [-E_a/RT]$			VTF regime $\sigma T = \sigma_0 \exp [-B/R(T-T_0)]$			
			$\log(\sigma_0)$ (S.K.cm ⁻¹)	E_a (eV)	r^2	$\log(\sigma_0)$ (S.K.cm ⁻¹)	B (eV)	T_0 (°C)	r^2
$\beta-\text{La}_{1.7}\text{Bi}_{0.3}\text{Mo}_2\text{O}_9$	5h 875°C	98(1)	7.74	1.27	0.9999	3.84	0.21	246	0.9996
$\beta-\text{La}_{1.85}\text{Ba}_{0.15}\text{Mo}_2\text{O}_{8.925}$	12h 1000°C	94(2)	7.90	1.31	0.9999	5.24	0.39	144	0.9997

3. Comparison of the temperature dependences of the "free" cell volumes V_F deduced from the analysis of neutron diffraction patterns and of complex impedance spectra for $\beta\text{-La}_{1.85}\text{Ba}_{0.15}\text{Mo}_2\text{O}_{8.925}$ and $\beta\text{-La}_{1.7}\text{Bi}_{0.3}\text{Mo}_2\text{O}_9$ compounds.

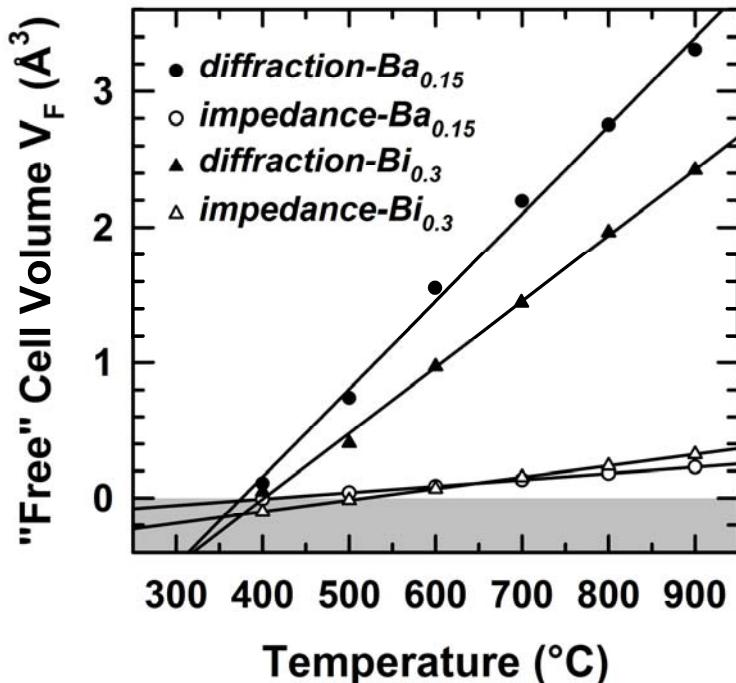


Figure S3

4. Comparison of the fraction of non-occupied volume in $\beta\text{-La}_{1.7}\text{Bi}_{0.3}\text{Mo}_2\text{O}_9$ and in $\beta\text{-La}_{1.85}\text{Ba}_{0.15}\text{Mo}_2\text{O}_{8.925}$ above 400°C to that determined in $\beta\text{-La}_2\text{Mo}_2\text{O}_9$ at 670°C.

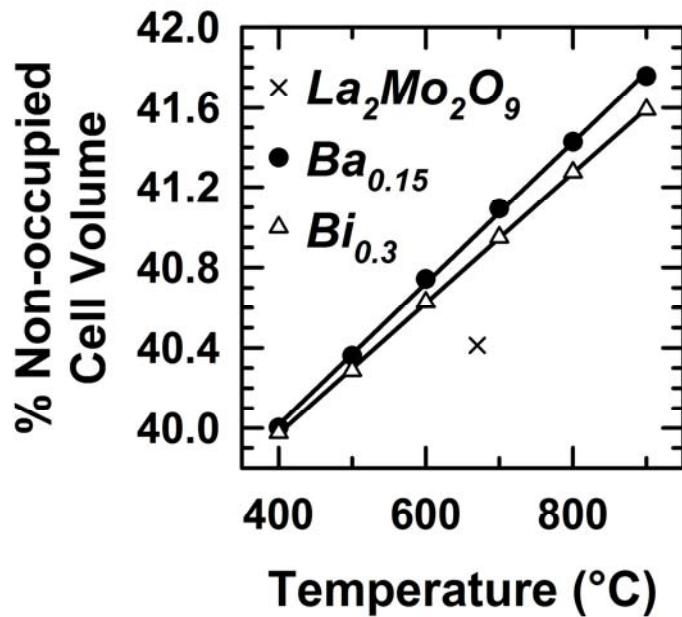


Figure S4