Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Structural origin of the enhanced ionic conductivity upon Nb doping in $Sr_{11}Mo_4O_{23}$ defective double perovskite

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Figures

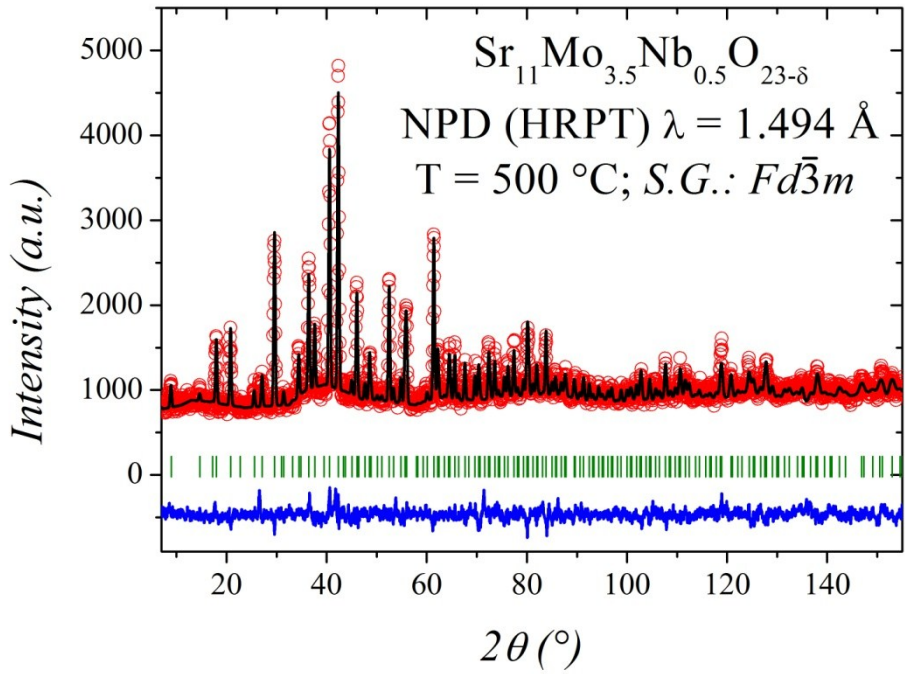

Figure S1: Observed (circles), calculated (full line) and difference (bottom) Rietveld profiles at 500 °C for $Sr_{11}Mo_{3.5}Nb_{0.5}O_{23-\delta}$ after NPD refinement.

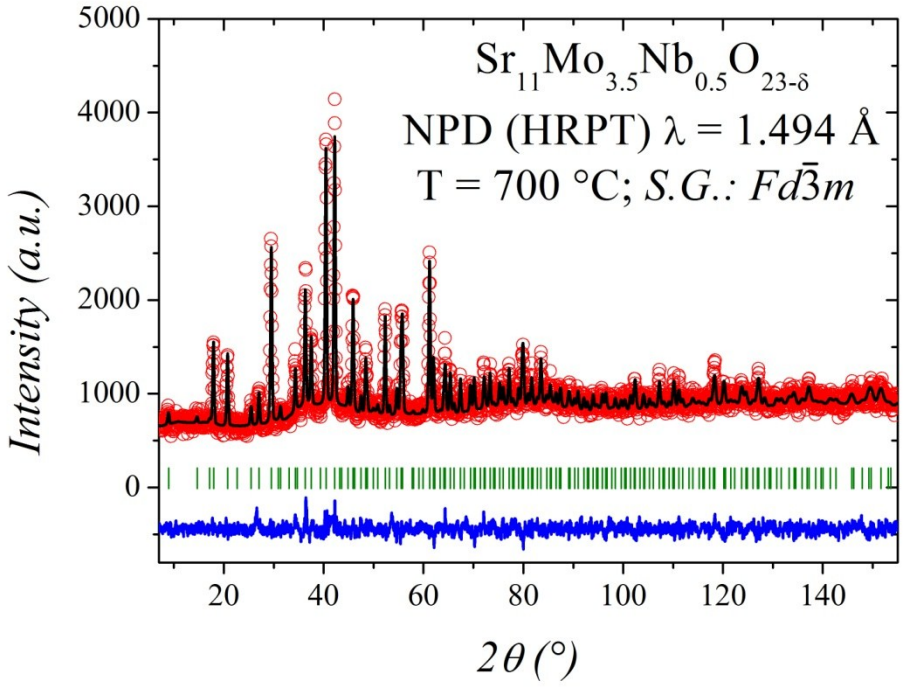

Figure S2: Observed (circles), calculated (full line) and difference (bottom) Rietveld profiles at 700 °C for $Sr_{11}Mo_{3.5}Nb_{0.5}O_{23-\delta}$ after NPD refinement.

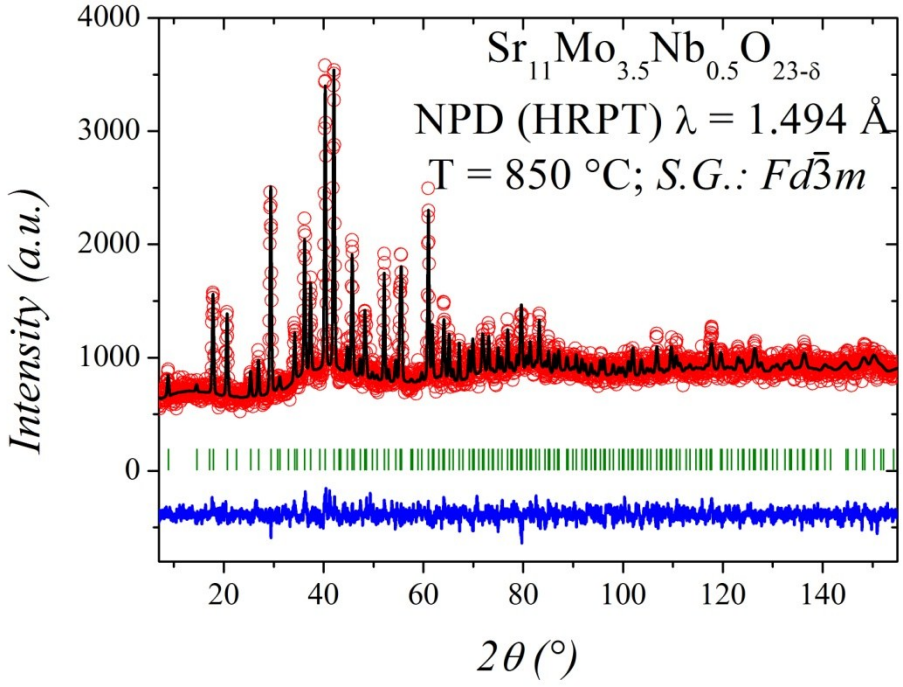

Figure S3: Observed (circles), calculated (full line) and difference (bottom) Rietveld profiles at 850 °C for $Sr_{11}Mo_{3.5}Nb_{0.5}O_{23-\delta}$ after NPD refinement.

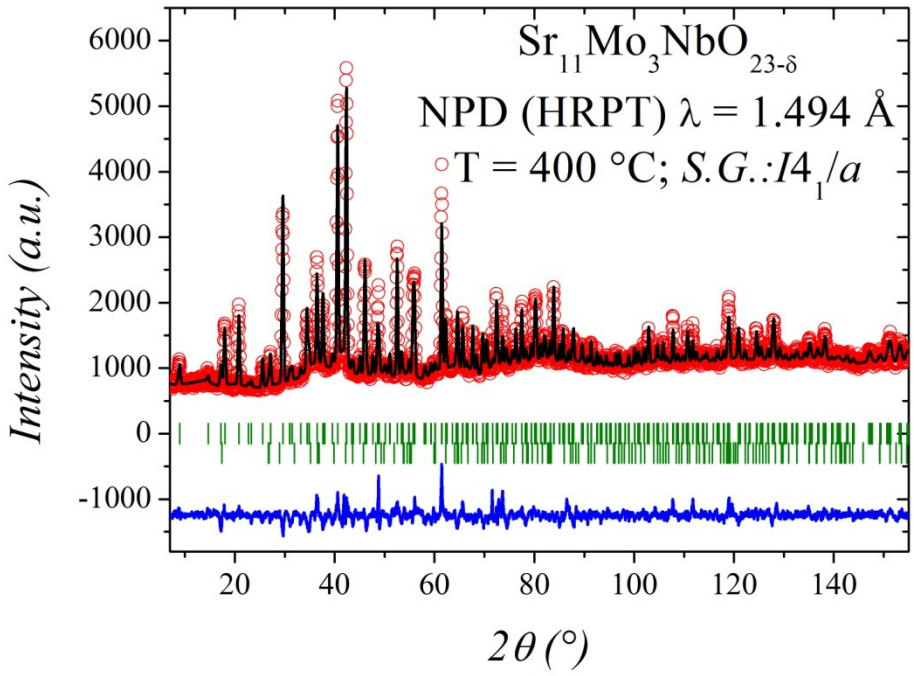

Figure S4: Observed (circles), calculated (full line) and difference (bottom) Rietveld profiles at 400 °C for $Sr_{11}Mo_3NbO_{23-\delta}$ after NPD refinement.

Tables

Table S1: Crystallographic parameters for $Sr_{11}Mo_{3.5}Nb_{0.5}O_{23-\delta}$ phase from NPD data at 500 °C. System: Cubic, Space group: $Fd\bar{3}m$, Z = 8. Unit-cell parameters: *a* = 16.5510(7) Å, and V = 4533.9(3) Å^3.

Atom		x	y	z	B_{iso}(Å^2)	Occ
Sr1	8*b*	0.375	0.375	0.375	7.9(9)	1
Sr2	48*f*	0.4004(1)	0.125	0.125	3.1(1)	1
Sr3	32*e*	0.2290(3)	0.2290(3)	0.2290(3)	4.2(2)	1
Mo1	16*d*	0.5	0.5	0.5	1.2(2)	1
Mo2	16*c*	0	0	0	3.0(2)	0.75
Nb2	16*c*	0	0	0	3.0(2)	0.25
O1	96*g*	0.5011(4)	0.5011(4)	0.6169(4)	3.7(1)	1
O2	96*g*	0.0802(7)	0.0802(7)	-0.014(2)		0.48(2)
O3	96*h*	0	-0.0802(9)	0.0802(9)	3.2(7)	0.24(1)
O4	96*g*	0.977(1)	0.977(1)	0.112(2)	4.5(9)	0.22(1)
	Anisotropic displacement parameters					
O2		β11 x10^4 β12 x10^4 126(10) -79(11)	β22 x10^4 β13 x10^4 126(10) 48(7)	β33 x10^4 β23 x10^4 130(11) 48(7)		

NPD: R_p: 4.4%; R_{wp}: 5.7%; R_{exp}: 4.8%; χ^2: 1.4; R_{Bragg}: 12.0%

Table S2: Crystallographic parameters for $Sr_{11}Mo_{3.5}Nb_{0.5}O_{23-\delta}$ phase from the NPD data at 700 °C. System: Cubic, Space group: $Fd\bar{3}m$, Z = 8. Unit-cell parameters: *a* = 16.598(1) Å, and V = 4572.7(6) Å^3.

Atom		x	y	z	B_{iso}(Å^2)	Occ
Sr1	8*b*	0.375	0.375	0.375	5.9(8)	1
Sr2	48*f*	0.4025(1)	0.125	0.125	2.0(1)	1
Sr3	32*e*	0.2273(4)	0.2273(4)	0.2273(4)	4.3(3)	1
Mo1	16*d*	0.5	0.5	0.5	0.4(1)	1
Mo1	16*c*	0	0	0	3.8(3)	0.75
Nb2	16*c*	0	0	0	3.8(3)	0.25
O1	96*g*	0.5026(4)	0.5026(4)	0.6173(4)	4.0(1)	1
O2	96*g*	0.0807(6)	0.0807(6)	-0.015(2)		0.44(2)
O3	96*h*	0	-0.078(1)	0.078(1)	6.0(9)	0.29(2)
O4	96*g*	0.981(1)	0.981(1)	0.110(2)	6.0(9)	0.29(2)
	Anisotropic displacement parameters					
O2		β11 x10^4 β12 x10^4 44(8) -27(7)	β22 x10^4 β13 x10^4 44(8) 51(6)	β33 x10^4 β23 x10^4 182(7) 51(6)		

NPD: R_p: 5.3%; R_{wp}: 6.6%; R_{exp}: 5.9%; χ^2: 1.3; R_{Bragg}: 10.7%

Table S3: Crystallographic parameters for $Sr_{11}Mo_{3.5}Nb_{0.5}O_{23-\delta}$ phase from the NPD data at 850 °C. System: Cubic, Space group: $Fd\bar{3}m$, Z = 8. Unit-cell parameters: *a* = 16.649(2) Å, and V = 4614.8(7) Å^3.

Atom		x	y	z	B_{iso}(Å^2)	Occ
Sr1	8*b*	0.375	0.375	0.375	6.2(8)	1
Sr2	48*f*	0.4028(1)	0.125	0.125	2.6(1)	1
Sr3	32*e*	0.2271(4)	0.2271(4)	0.2271(4)	5.7(3)	1
Mo1	16*d*	0.5	0.5	0.5	0.2(1)	1
Mo1	16*c*	0	0	0	4.9(4)	0.75
Nb2	16*c*	0	0	0	4.9(4)	0.25
O1	96*g*	0.4995(5)	0.4995(5)	0.6159(5)	4.3(2)	1
O2	96*g*	0.0784(7)	0.0784(7)	-0.016(2)		0.51(2)
O3	96*h*	0	-0.078(1)	0.078(1)	6.0(9)	0.27(2)
O4	96*g*	0.983(1)	0.983(1)	0.112(2)	1.0(9)	0.14(2)
	Anisotropic displacement parameters					
O2		$\beta11$ x10^4 $\beta12$ x10^4 84(12) -60(11)	$\beta22$ x10^4 $\beta13$ x10^4 84(12) 38(7)	$\beta33$ x10^4 $\beta23$ x10^4 149(11) 38(7)		

NPD: R_p: 5.0%; R_{wp}: 6.4%; R_{exp}: 5.9%; χ^2: 1.2; R_{Bragg}: 10.6%

Table S4: Crystallographic parameters for $Sr_{11}Mo_3NbO_{23-\delta}$ phase from the NPD data at 400 °C. System: Tetragonal, Space group: $I4_1/a$, Z = 4. Unit-cell parameters: a = 11.6967(4) Å, c = 16.533(1) Å and V = 2262.0(2) Å^3.

Atom		x	y	z	B_{iso}(Å^2)	Occ
Sr1	4*a*	0	0.25	0.125	3.4(4)	1
Sr2	8*e*	0.5	0.25	0.603(2)	3.0(5)	1
Sr3	16*f*	0.224(2)	0.971(1)	0.879(1)	2.1(2)	1
Sr4	16*f*	0.216(1)	0.255(2)	0.524(1)	3.0(2)	1
Mo1	8*c*	0	0	0	0.8(1)	1
Mo2	8*d*	0	0	0.5	1.8(2)	0.5
Nb2	8*d*	0	0	0.5	1.8(2)	0.5
O1	16*f*	0.876(2)	0.144(2)	0.251(2)	2.0(4)	1
O2	16*f*	0.644(2)	0.127(2)	0.247(2)	2.8(5)	1
O3	16*f*	0.246(2)	0.254(3)	0.370(1)	4.1(5)	1
O4	16*f*	0.836(2)	0.160(2)	0.670(1)	1.7(2)	0.79(2)
O5	16*f*	0.873(2)	0.070(2)	0.528(2)	4.0(4)	0.87(3)
O6	16*f*	0.328(2)	0.300(2)	0.662(2)	4.0(4)	0.80(4)

NPD: R_p: 4.5%; R_{wp}: 6.0%; R_{exp}: 3.7%; χ^2: 2.6; R_{Bragg}: 11.7%