

Supporting Information

Bimetallic Fe-Ni exsolution from A site deficient SrTiO₃: insight into the reciprocal role of metal active centers

Pietro Mariani^a, Jacopo Orsilli^{a,b}, Simone Mascotto^c, Henk Stoffel^c, Damiano Monticelli^d, Enrico Berretti^e, Alessandro Lavacchi^e, Luca Bignardi, Cinzia Cepek^f, Maria A. Goula^g, Nikolaos D. Charisiou^g, Angeliki I. Latsiou^g, Silvia Mostoni^a, Barbara Di Credico^a, Roberto Scotti^a and Massimiliano D'Arienzo^{a*}

ICP analysis

Table S1: ICP analysis on synthesized doped and co-doped perovskites.

Sample	Fe (mol% Sr)	Ni (mol% Sr)
1Fe-STO	1.02	0.01
5Fe-STO	5.06	0.01
1Ni-STO	0.03	0.95
5Ni-STO	0.25	4.56
5Fe5Ni-STO	5.33	4.48
5Fe0.1Ni-STO	5.11	0.12

XAS analysis

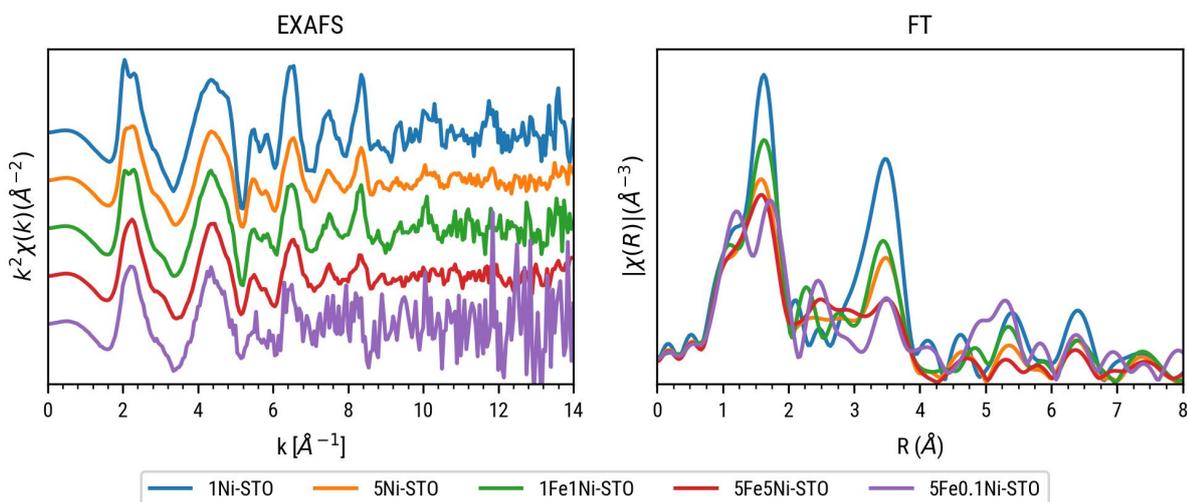


Figure S1: Comparison of the EXAFS signal, left, and its Fourier Transform, right, of the as prepared samples at the Ni K-edge.

Table S2: Results of the LCF on the Fe and Ni K-edges of the samples heated at 600 and 900°C, using the as prepared samples (AP) and pure metals as references.

<i>Sample</i>	400°C		600°C		900°C		<i>Sample</i>	400°C		600°C		900°C	
<i>Fe edge</i>	AP	Met	AP	Met	AP	Met	<i>Ni edge</i>	AP	Met	AP	Met	AP	Met
<i>1Fe-STO</i>	92	11	90	13	79	24	<i>1Ni-STO</i>	94	0	86	10	74	23
<i>5Fe-STO</i>	90	11	89	12	74	28	<i>5Ni-STO</i>	92	2	80	16	55	45
<i>1Fe1Ni-STO</i>	89	14	88	16	79	22	<i>1Fe1Ni-STO</i>	95	0	68	30	43	58
<i>5Fe5Ni-STO</i>	90	11	87	15	77	25	<i>5Fe5Ni-STO</i>	89	7	63	36	33	70
<i>5Fe0.1Ni-STO</i>	96	4	94	7	78	21	<i>5Fe0.1Ni-STO</i>	94	1	68	32	36	67

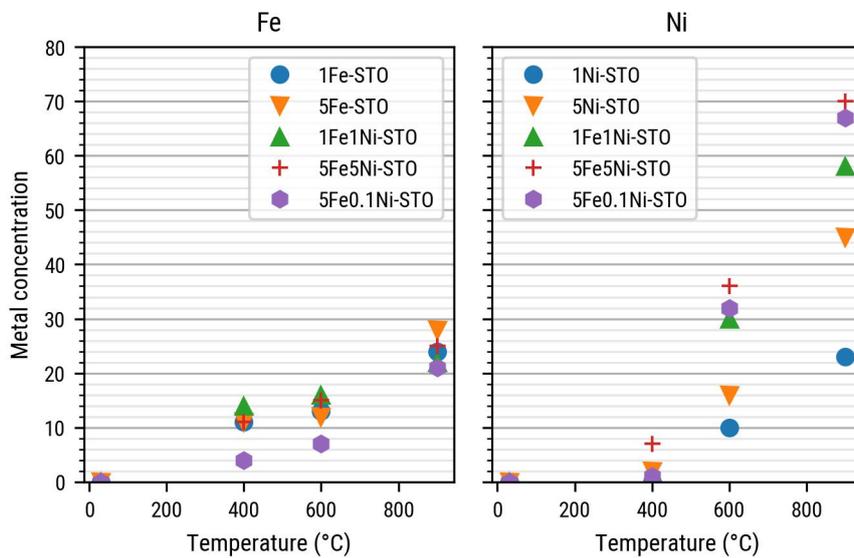


Figure S2: Evolution of the metal concentration in the STO samples heated at different temperatures.

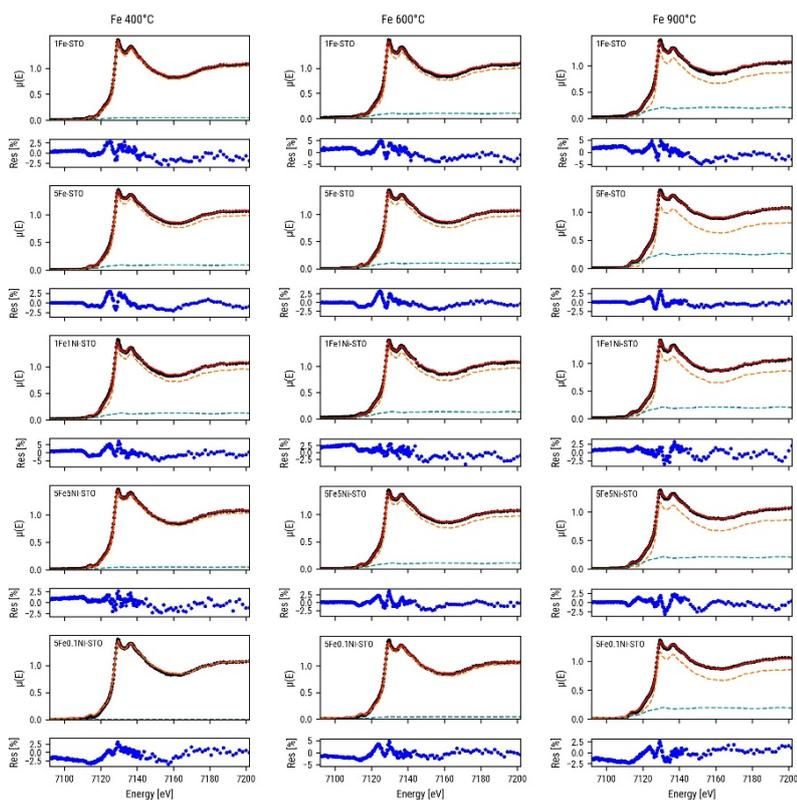


Figure S3: LCF of the Fe spectra collected after heating at 400°C, 600°C and 900°C. Black scatter plot: data, red plot: fit, green-dashed plot: metallic Fe, orange-dashed plot: AP spectrum, blue scatter plot: residuals.

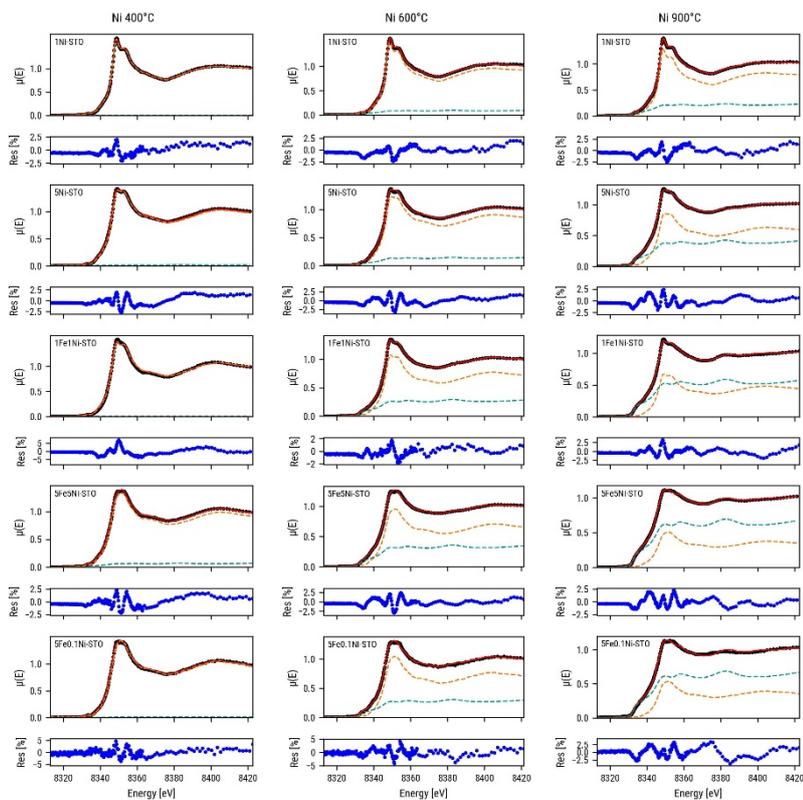


Figure S4: LCF of the Ni spectra collected after heating at 400°C, 600°C and 900°C. Black scatter plot: data, red plot: fit, green-dashed plot: metallic Fe, orange-dashed plot: AP spectrum, blue scatter plot: residuals.

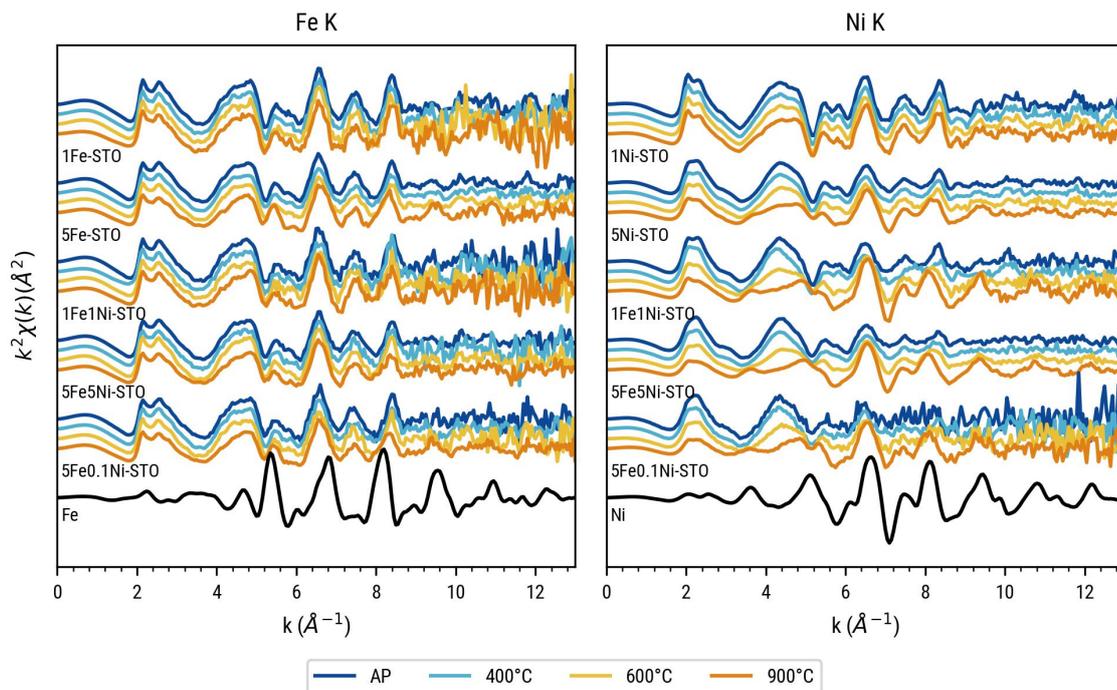


Figure S5: EXAFS spectra of the samples recorded at the Fe K-edge (column left) and Ni K-edge (column on the right). (e0 set for both at the metal edges, 7112 and 8333 eV). In black the spectra of the metal.

Table S3: Interatomic Ni distances calculated for the as prepared (AP) samples and after heating at 900°C (in brackets the error on the last digit).

<i>Sample</i>	Distance (Å)						
	Ni-O	Ni-Sr	Ni-Ti	Ni-Ni	Ni-Ni (2)	Ni-Ni (3)	Ni-Ni (4)
<i>1Ni-STO AP</i>	2.03(2)	3.35(2)	3.87(2)	-	-	-	-
<i>1Ni-STO 400</i>	2.03(2)	3.37(2)	3.85(2)	-	-	-	-
<i>1Ni-STO 600</i>	2.03(2)	3.37(2)	3.86(2)	-	-	-	-
<i>1Ni-STO 900</i>	2.02(2)	3.36(2)	3.86(2)	2.48(2)	-	-	-
<i>5Ni-STO 900</i>	2.03(2)	3.3(2)	3.9(1)	2.48(2)	3.51(4)	4.30(4)	-
<i>1Fe1Ni-STO 900</i>	2.02(2)	3.3(2)	3.9(1)	2.49(2)	3.53(4)	4.32(4)	-
<i>5Fe5Ni-STO 900</i>	-	-	-	2.49(2)	3.52(4)	4.31(4)	4.98(6)
<i>5Fe0.1Ni-STO 900</i>	-	-	-	2.49(2)	3.53(4)	4.32(4)	-

Table S4: Interatomic Fe distances calculated for the as prepared (AP) samples and after heating at 900°C (in brackets the error on the last digit).

<i>Sample</i>	Distance (Å)					
	Fe-O	Fe-Sr	Fe-Ti	Fe-Fe	Fe-Fe (2)	Fe-Fe (3)
<i>1Fe-STO AP</i>	1.99(2)	3.36(3)	4.0(1)			
<i>1Fe-STO 400</i>	1.99(2)	3.38(3)	3.9(1)			
<i>1Fe-STO 600</i>	1.99(2)	3.34(3)	3.9(1)			
<i>1Fe-STO 900</i>	2.00(2)	3.35(2)	3.9(1)	2.4(2)		
<i>5Fe-STO 900</i>	1.96(2)	3.35(2)	3.88(2)	2.45(2)	2.83(2)	4.00(3)
<i>1Fe1Ni-STO 900</i>	2.0(1)	3.4(2)	3.9(2)	2.5(2)		
<i>5Fe5Ni-STO 900</i>	1.97(2)	3.35(3)	3.9(1)	2.48(2)	2.86(2)	4.0(1)
<i>5Fe0.1Ni-STO 900</i>	1.96(2)	3.35(2)	2.89(2)	2.45(2)	2.83(4)	4.00(4)

XPS analysis

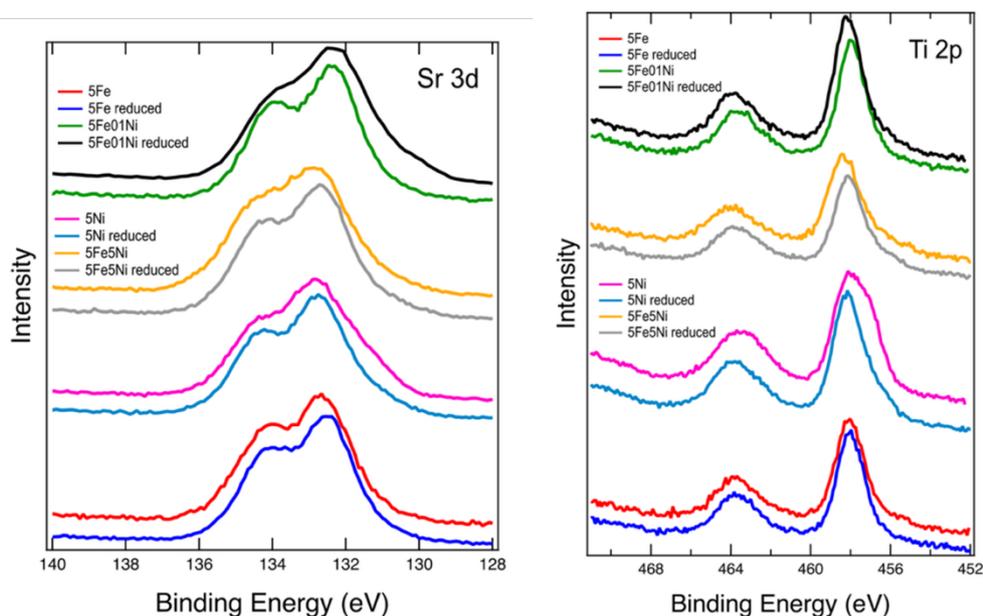


Figure S6: XPS core levels spectra of: Sr 3d (Left) and Ti 2p (Right)). The intensities of all the spectra have been normalized to the total Ti 2p intensity.

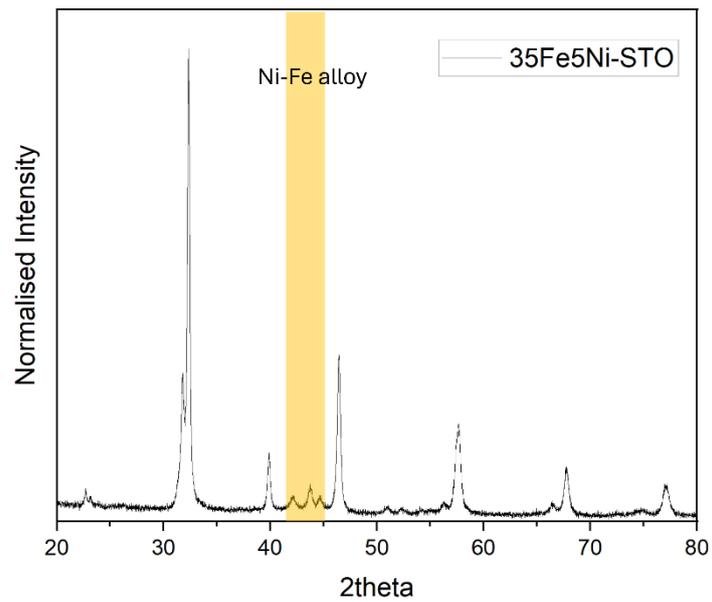


Fig. S7: PXR D of 35Fe5Ni-STO after exsolution at 900°C for 2h. Highlighted are the peaks of different composition of Ni-Fe alloy