Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Influence of crystal structure on the electrochemical performance of A-site-deficient $Sr_{1-s}Nb_{0.1}Co_{0.9}O_{3-\delta}$ perovskite cathodes

Yinlong Zhu,[a] Ye Lin,[b] Xuan Shen,[c,d] Jaka Sunarso,[e] Wei Zhou*[f] Shanshan Jiang,[a] Dong Su,[c] Fanglin Chen,[b] and Zongping Shao*[g]

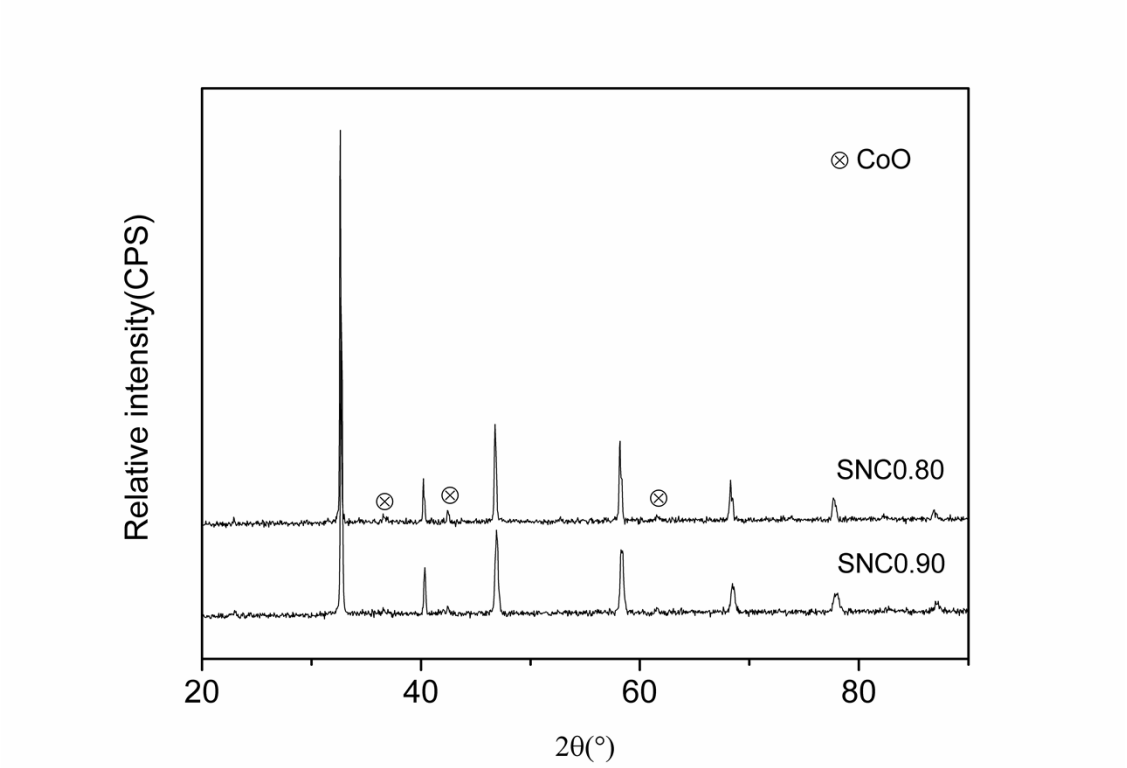

Fig. S1. XRD patterns of SNC0.90 and SNC0.80 powders synthesized at 1200 °C.

Table S1. The reliability factors of Le Bail refinements on XRD patterns of SNC0.98 using model based on Pm-3m, P4mm and P4mm space group.

Phase model	R_{wp} (%)	R_p (%)	χ^2
Pm-3m	3.70	2.86	1.26
P4mm	3.40	2.64	1.16
P4/mmm	3.54	2.77	1.22

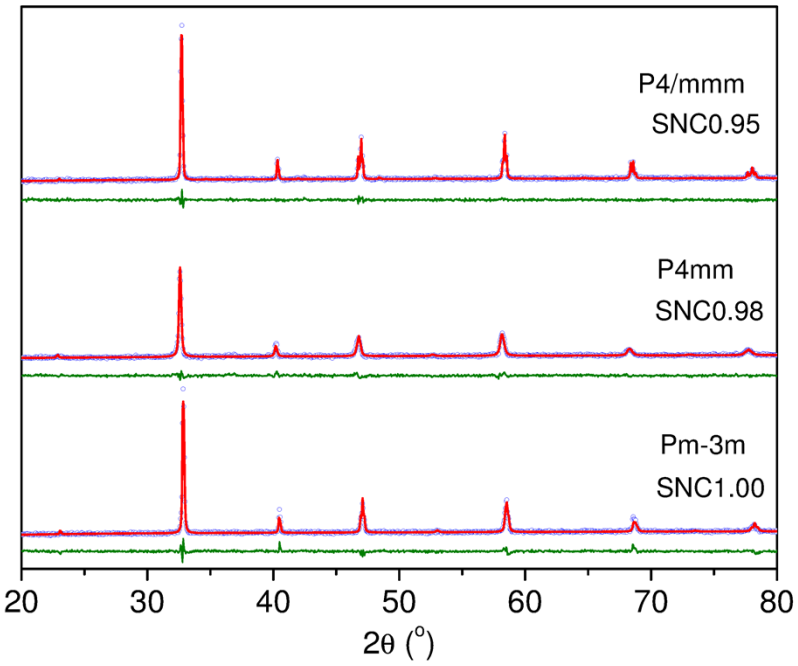

Fig. S2. Reitveld refinements of SNC1.00, SNC0.98 and SNC0.95 XRD patterns.

Table S2. Lattice parameters of SNC1.00, SNC0.98 and SNC0.95 based on Rietveld refinement.

SNC1.00		SNC0.98		SNC0.95	
Pm-3m		P4mm		P4/mmm	
a	3.873(19)	a	3.879(02)	a	3.870(55)
		c	3.892(20)	c	7.777(97)
Sr		Sr		Sr	
x	0.5	x	0	x	0.5
y	0.5	y	0	y	0.5
z	0.5	z	0	z	0.26186
Occ	1.0	Occ	0.98	Occ	0.95
Co/Nb		Co/Nb		Co1/Nb1	
x	0.0	x	0.5	x	0
y	0.0	y	0.5	y	0
z	0.0	z	0.52804	z	0
Occ	0.9/0.1	Occ	0.9/0.1	Occ	0.9/0.1
O1		O1		Co2/Nb2	
x	0.5	x	0.5	x	0
y	0.0	y	0.5	y	0
z	0.0	z	0.00006	z	0.5
Occ	1	Occ	1	Occ	0.9/0.1
		O2		O1	
		x	0.5	x	0.5
		y	0	y	0
		z	0.41723	z	0
		Occ	1	Occ	1
				O2	
				x	0
				y	0
				z	0.74187
				Occ	1
				O3	
				x	0.5
				y	0
				z	0.5
				Occ	1
Reliability factors (%)					
R_p	3.11	R_p	2.81	R_p	2.52
R_{wp}	4.44	R_{wp}	3.61	R_{wp}	3.18
χ^2	1.48	χ^2	1.23	χ^2	1.12

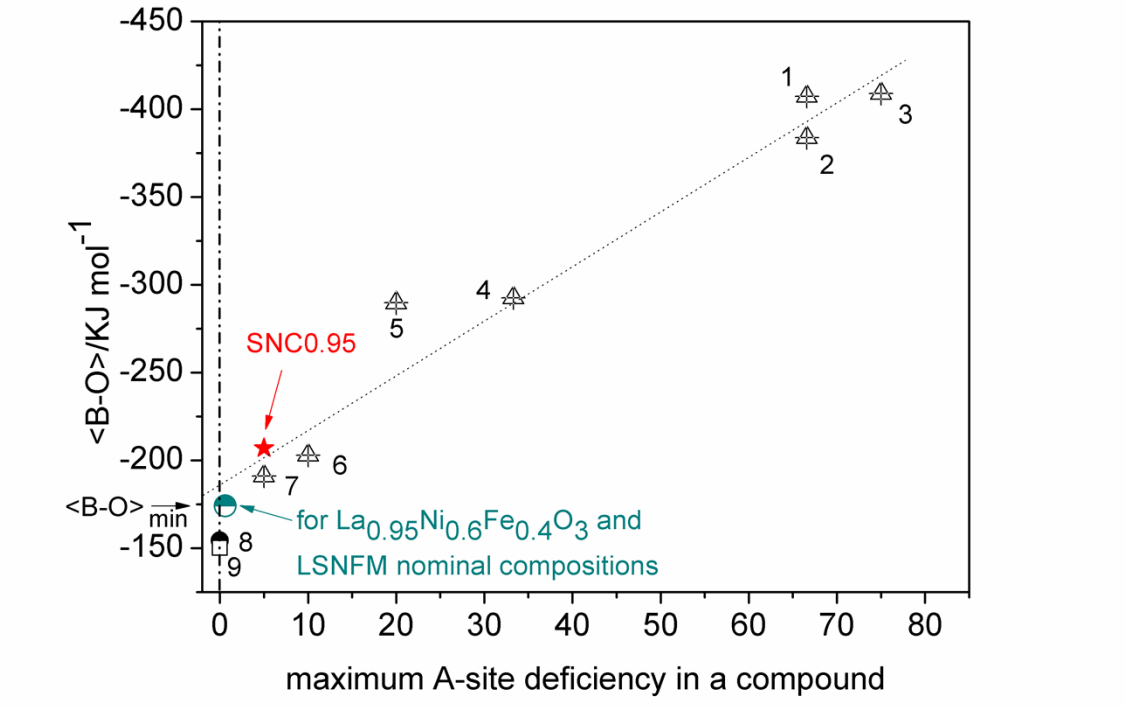

Fig. S3. Average B(B', B")-O (B-O) bond energy between the B and oxygen sublattices estimated from the thermodynamic data for 1. $La_{1/3}TaO_3$; 2. $La_{1/3}NbO_3$; 3. $Na_{0.25}WO_3$; 4. $La_{2/3}(Ti^{4+}_{0.5}Ti^{3+}_{0.5})O_{3-\delta}$; 5. $La_{0.2}Sr_{0.6}Ti_{0.8}Nb_{0.2}O_3$; 6. $La_{0.9}(Mn^{4+}_{0.5}Mn^{3+}_{0.5})O_{3-\delta}$; 7. $La_{0.55}Sr_{0.4}Co^{3+}_{0.2}Fe^{3+}_{0.8}\ O_3$; 8. $LaNiO_{3-\delta}$; 9. $LaCoO_{3-\delta}$. The data except SNC0.95 are extracted from Ref [1].

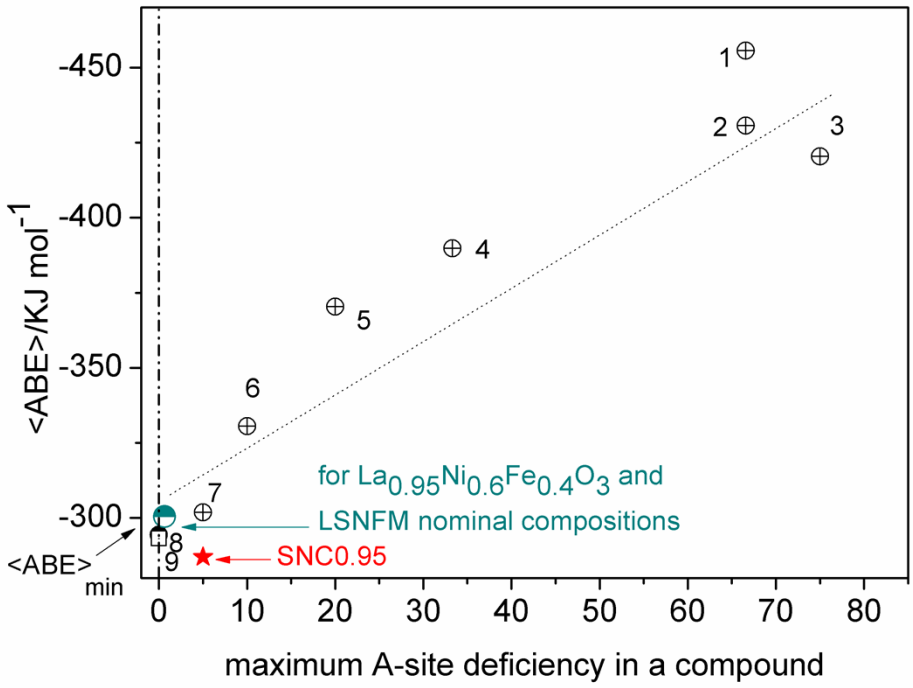

Fig. S4. Average metal (A, B)-oxygen bond energy within the perovskite lattice (<ABE>) estimated from the thermodynamic data for 1. $La_{1/3}TaO_3$; 2. $La_{1/3}NbO_3$; 3. $Na_{0.25}WO_3$; 4. $La_{2/3}(Ti^{4+}_{0.5}Ti^{3+}_{0.5})O_{3-\delta}$; 5. $La_{0.2}Sr_{0.6}Ti_{0.8}Nb_{0.2}O_3$; 6. $La_{0.9}(Mn^{4+}_{0.5}Mn^{3+}_{0.5})O_{3-\delta}$; 7. $La_{0.55}Sr_{0.4}Co^{3+}_{0.2}Fe^{3+}_{0.8}O_3$; 8. $LaNiO_{3-\delta}$; 9. $LaCoO_{3-\delta}$. The data except SNC0.95 are extracted from Ref [1].

Figure S2 and Figure S3 illustrate the correlation between the maimum A-site deficiency in compounds (data were extracted from the literature **[1]**) and the average B(B', B")-O (<B-O>) bond energy or average metal (A, B)-oxygen bond energy within the perovskite lattice (<ABE>) estimated from the thermodynamic data. **[2]** The method of calculating <A-O>, <B-O> and <ABE> for a cation stoichiometric $A_{1-x}A'_xB_{1-y-z}B'_yB''_zO_3$ and for A-site deficient ($(A_{1-x}A'_x)_sB_{1-y-z}B'_yB''_zO_3$) compositions were described as follows:**[3]**

(the following equations applied to A', B' and B" are similar to A and B)

$$<ABE>=<A\text{-}O>+<B\text{-}O> \quad (1)$$

$$<A\text{-}O>=\Delta(A\text{-}O)+\Delta(A'\text{-}O) \quad (2)$$

$$<B\text{-}O>=\Delta(B\text{-}O)+\Delta(B'\text{-}O)+\Delta(B''\text{-}O) \quad (3)$$

$$\Delta(A\text{-}O)=x_A/(CN_A*m)*(\Delta H_{AmOn}-m*\Delta H_A-n/2*D_{O2}) \quad (4a)$$

$$\Delta(A\text{-}O)=x_A*s/(CN_A*m)*(\Delta H_{AmOn}-m*\Delta H_A-n/2*D_{O2})$$

(in the case of A-site deficiency) (4b)

$$\Delta(B\text{-}O)=x_B/(CN_B*m)*(\Delta H_{BmOn}-m*\Delta H_B-n/2*D_{O2}) \quad (5)$$

Some parameters of above equations are explained as:

x_A and x_B : the molar fraction of A and B metals;
s: the fraction of A-site deficiency compositions $(A_{1-x}A'_x)_sB_{1-y-z}B'_yB''_zO_3(s<1)$;
$\Delta H_{A(B)mOn}$ and$\Delta H_{A(B)}$: the enthalpy of formation of one mole of A(B)mOn oxides and the sublimation energy of A(B) metal at 25 ^oC; **[2]**
$CN_{A(B)}$: the coordination number of cations on the A and B sites;
D_{O2}: the dissociation energy of O_2 (500.2 kJ mol^{-1})

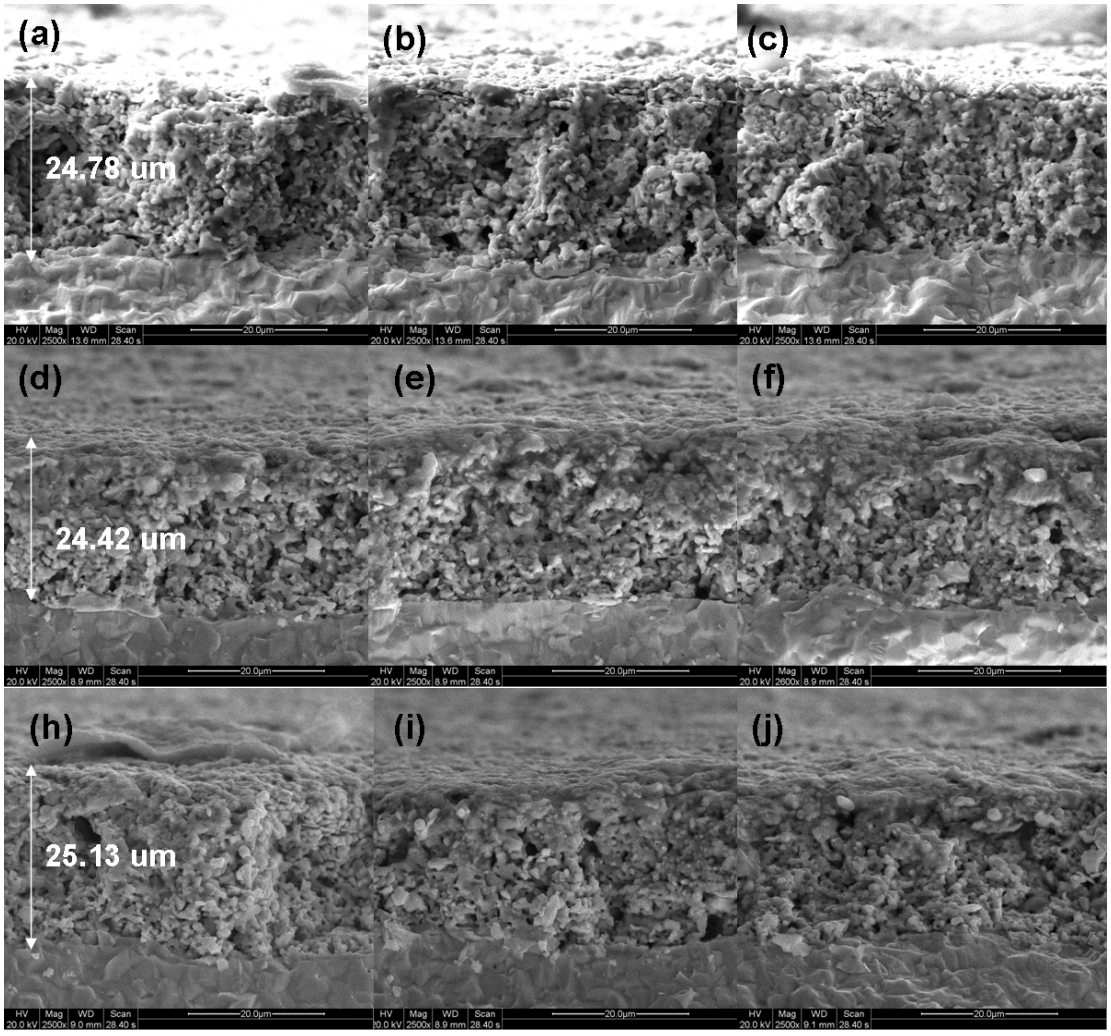

Fig. S5. SEM images of (a, b, c) SNC1.00, (d, e, f) SNC0.98 and (h, i, j) SNC0.95 cathodes calcined at 1000 °C for 2 h in air after test. The scale bars of all images are 20 μm.

1. Konysheva, E.; Xu, X. X.; Irvine, J. T. S. *Adv. Mater.* **2012**, *24*, 528.
2. Kubaschewski, O,; Alcock, C. B. *Metallurgical Thermochemistry*, 5th Ed., Pergamon Press Ltd., Oxford, UK **1979,** p.391.
3. Voorhoeve, R. J. H.; Remeika, J. P.; Trimbe, L. E. *Ann. N. Y. Acad. Sci.* **1976**, *272*, 3.