

Effect of Substitution of *B*-sites by Mn, Fe and Co in Double Perovskite-type $\text{Ba}_3\text{CaNb}_2\text{O}_9$ on Structure and Electrical Properties

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Supporting information

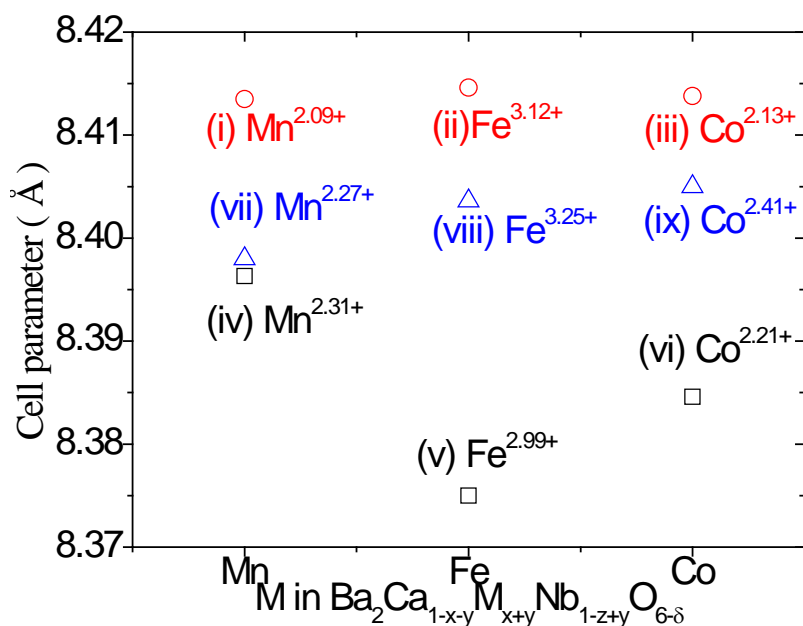


Fig. S1. The cell parameters of the as-prepared (i) $\text{Ba}_2\text{Ca}_{0.79}\text{Mn}_{0.16}\text{Nb}_{1.05}\text{O}_{5.60}$; (ii) $\text{Ba}_2\text{Ca}_{0.79}\text{Fe}_{0.16}\text{Nb}_{1.05}\text{O}_{5.68}$; (iii) $\text{Ba}_2\text{Ca}_{0.79}\text{Co}_{0.16}\text{Nb}_{1.05}\text{O}_{5.61}$; (iv) $\text{Ba}_2\text{Ca}_{0.67}\text{Mn}_{0.33}\text{NbO}_{5.55}$; (v) $\text{Ba}_2\text{Ca}_{0.67}\text{Fe}_{0.33}\text{NbO}_{5.66}$; (vi) $\text{Ba}_2\text{Ca}_{0.67}\text{Co}_{0.33}\text{NbO}_{5.53}$; (vii) $\text{Ba}_2\text{Ca}_{0.79}\text{Mn}_{0.5}\text{Nb}_{0.71}\text{O}_{5.09}$; (viii) $\text{Ba}_2\text{Ca}_{0.79}\text{Fe}_{0.5}\text{Nb}_{0.71}\text{O}_{5.35}$; (ix) $\text{Ba}_2\text{Ca}_{0.79}\text{Co}_{0.5}\text{Nb}_{0.71}\text{O}_{5.10}$.

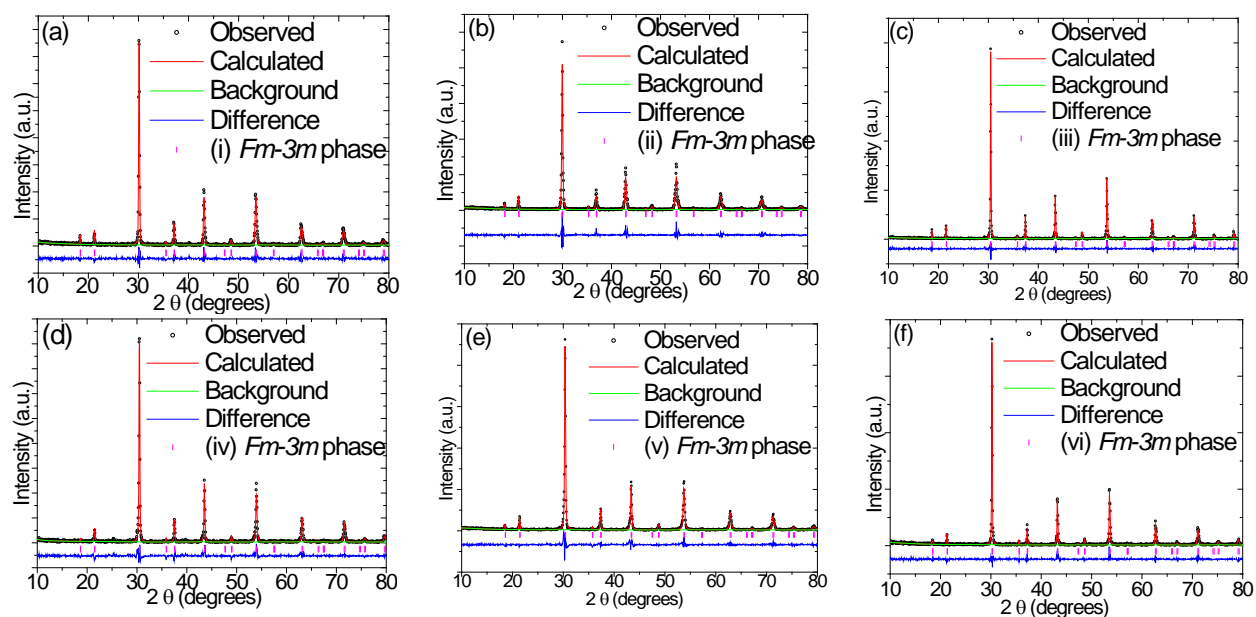


Fig. S2. Rietveld refinement of (a) $\text{Ba}_2\text{Ca}_{0.79}\text{Mn}_{0.16}\text{Nb}_{1.05}\text{O}_{5.60}$ (i); (b) $\text{Ba}_2\text{Ca}_{0.79}\text{Fe}_{0.16}\text{Nb}_{1.05}\text{O}_{5.68}$ (ii); (c) $\text{Ba}_2\text{Ca}_{0.79}\text{Co}_{0.16}\text{Nb}_{1.05}\text{O}_{5.61}$ (iii), (d) $\text{Ba}_2\text{Ca}_{0.67}\text{Mn}_{0.33}\text{NbO}_{5.55}$ (iv); (e) $\text{Ba}_2\text{Ca}_{0.67}\text{Fe}_{0.33}\text{NbO}_{5.66}$ (v) and (f) $\text{Ba}_2\text{Ca}_{0.67}\text{Co}_{0.33}\text{NbO}_{5.53}$ (vi), after explored in 5000 ppm $\text{H}_2\text{S}/\text{H}_2$ at 600 °C for 12h.

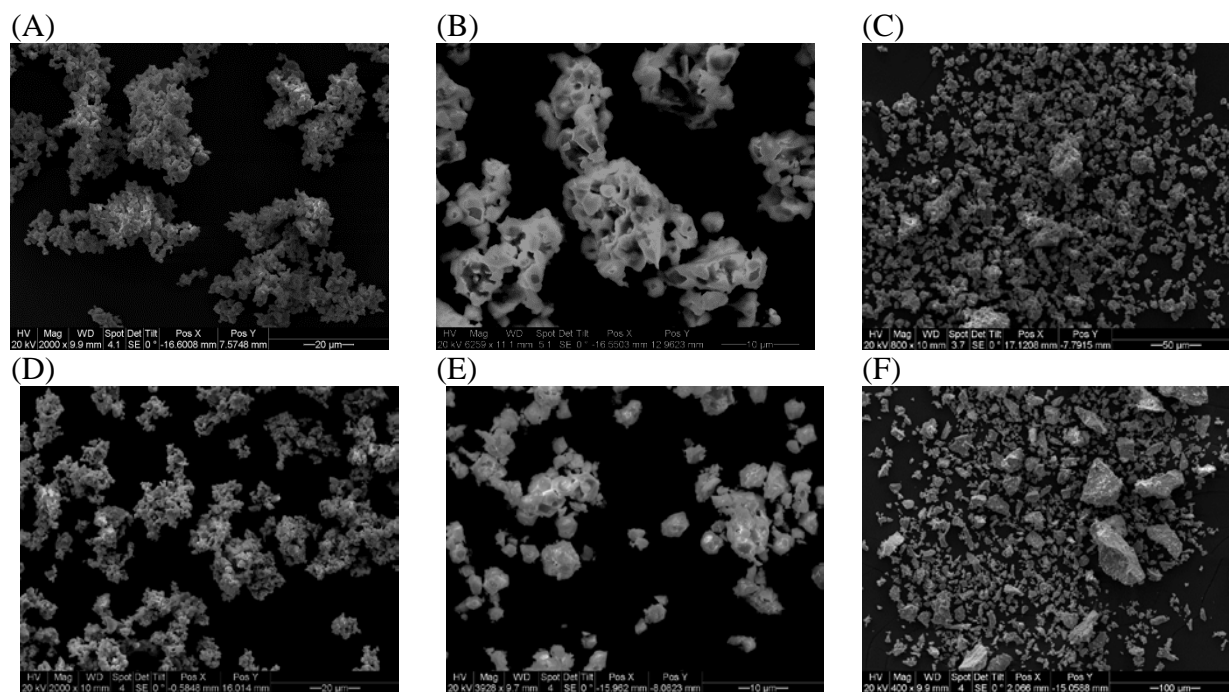


Fig. S3. Scanning electron microscopy (SEM) images of the representative as-prepared samples (A) $\text{Ba}_2\text{Ca}_{0.79}\text{Mn}_{0.16}\text{Nb}_{1.05}\text{O}_{5.60}$; (B) $\text{Ba}_2\text{Ca}_{0.79}\text{Fe}_{0.16}\text{Nb}_{1.05}\text{O}_{5.68}$; (C) $\text{Ba}_2\text{Ca}_{0.79}\text{Co}_{0.16}\text{Nb}_{1.05}\text{O}_{5.61}$, (D) $\text{Ba}_2\text{Ca}_{0.67}\text{Mn}_{0.33}\text{NbO}_{5.55}$; (E) $\text{Ba}_2\text{Ca}_{0.67}\text{Fe}_{0.33}\text{NbO}_{5.66}$; and (F) $\text{Ba}_2\text{Ca}_{0.67}\text{Co}_{0.33}\text{NbO}_{5.53}$, after explored in 5000 ppm $\text{H}_2\text{S}/\text{H}_2$ at 600 °C for 12h.

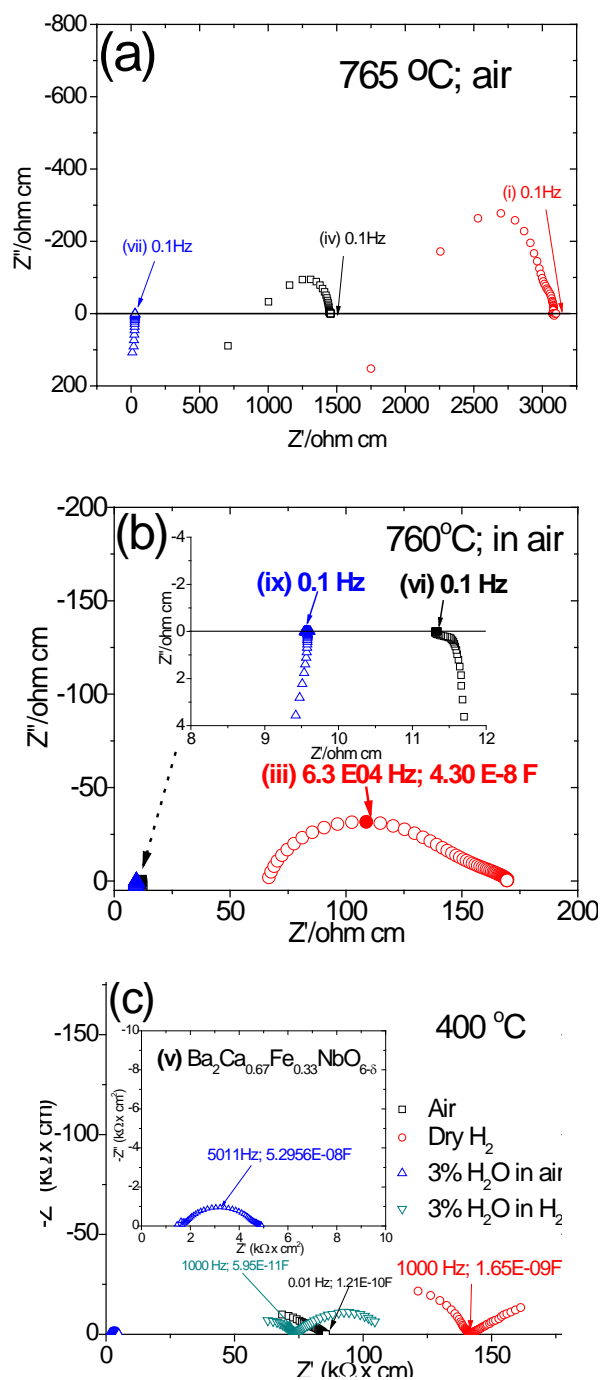


Fig. S4. The electrochemical impedance spectra of (a) $\text{Ba}_2\text{Ca}_{0.79}\text{Mn}_{0.16}\text{Nb}_{1.05}\text{O}_{5.60}$ (i), $\text{Ba}_2\text{Ca}_{0.67}\text{Mn}_{0.33}\text{NbO}_{5.55}$ (iv) and $\text{Ba}_2\text{Ca}_{0.79}\text{Mn}_{0.5}\text{Nb}_{0.71}\text{O}_{5.09}$ (vii), in air at 760 °C; (b) $\text{Ba}_2\text{Ca}_{0.79}\text{Co}_{0.16}\text{Nb}_{1.05}\text{O}_{5.61}$ (iii), $\text{Ba}_2\text{Ca}_{0.67}\text{Co}_{0.33}\text{NbO}_{5.53}$ (vi) and $\text{Ba}_2\text{Ca}_{0.79}\text{Co}_{0.5}\text{Nb}_{0.71}\text{O}_{5.10}$ (ix), in air at 765 °C and (c) $\text{Ba}_2\text{Ca}_{0.67}\text{Fe}_{0.33}\text{NbO}_{5.66}$ (v) in air, wet air, dry H_2 and wet H_2 at 400 °C.

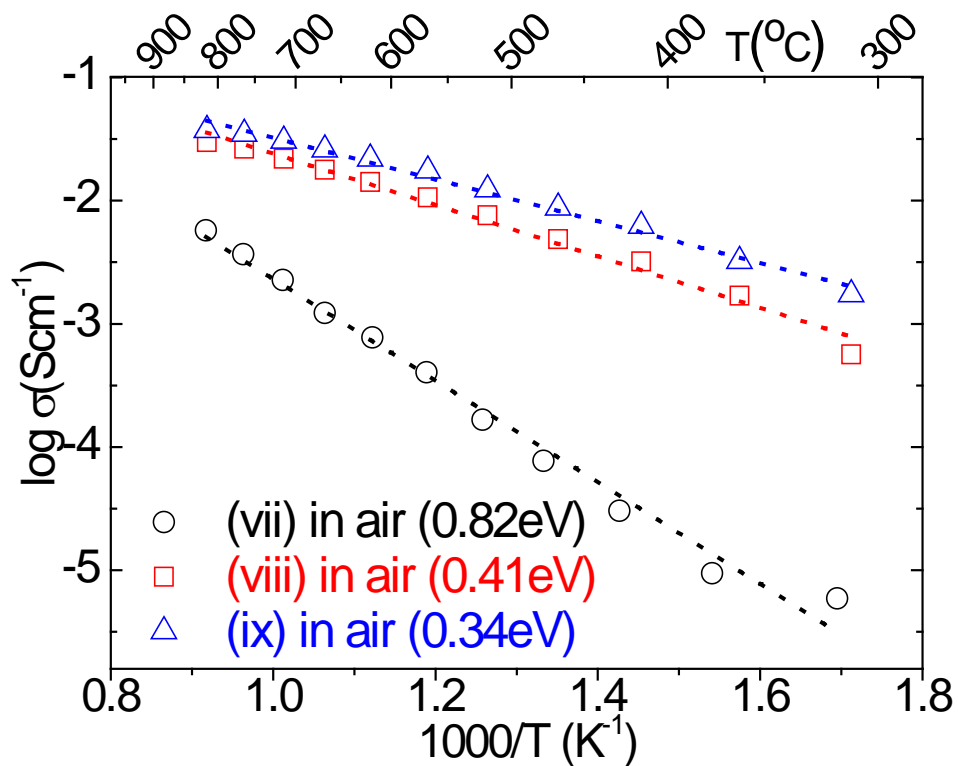


Fig. S5. The Arrhenius plot of $\text{Ba}_2\text{Ca}_{0.79}\text{Mn}_{0.5}\text{Nb}_{0.71}\text{O}_{5.09}$ (vii), $\text{Ba}_2\text{Ca}_{0.79}\text{Fe}_{0.5}\text{Nb}_{0.71}\text{O}_{5.09}$ (viii) and $\text{Ba}_2\text{Ca}_{0.79}\text{Co}_{0.5}\text{Nb}_{0.71}\text{O}_{5.09}$ (ix) in air.

Table S1. The EDX analysis of the as-prepared (i-ix) $\text{Ba}_2(\text{Ca}_{1-x-y}\text{M}_x\text{Nb}_y)(\text{Nb}_{1-z}\text{M}_z)\text{O}_{6-\delta}$ where M = Mn, Fe, Co.

Compounds	Cations	Experimental (As-prepared)	Theoretical
$\text{Ba}_2\text{Ca}_{0.79}\text{Mn}_{0.16}\text{Nb}_{1.05}\text{O}_{5.60}$	Ba	10.66	12.5
	Ca	3.76	4.94
	Nb	7.73	6.56
	Mn	1	1
$\text{Ba}_2\text{Ca}_{0.79}\text{Fe}_{0.16}\text{Nb}_{1.05}\text{O}_{5.68}$	Ba	12.16	12.5
	Ca	4.47	4.94
	Nb	6.47	6.56
	Fe	1	1
$\text{Ba}_2\text{Ca}_{0.79}\text{Co}_{0.16}\text{Nb}_{1.05}\text{O}_{5.61}$	Ba	10.96	12.5
	Ca	4.27	4.94
	Nb	7.27	6.56
	Co	1	1
$\text{Ba}_2\text{Ca}_{0.67}\text{Mn}_{0.33}\text{NbO}_{5.55}$	Ba	6.94	6.06
	Ca	1.96	2.03
	Nb	5.05	3.03
	Mn	1	1
$\text{Ba}_2\text{Ca}_{0.67}\text{Fe}_{0.33}\text{NbO}_{5.66}$	Ba	6.60	6.06
	Ca	2.04	2.03
	Nb	3.01	3.03
	Fe	1	1
$\text{Ba}_2\text{Ca}_{0.67}\text{Co}_{0.33}\text{NbO}_{5.53}$	Ba	6.72	6.06
	Ca	1.94	2.03
	Nb	4.01	3.03
	Co	1	1
$\text{Ba}_2\text{Ca}_{0.79}\text{Mn}_{0.5}\text{Nb}_{0.71}\text{O}_{5.09}$	Ba	3.76	4
	Ca	1.29	1.58
	Nb	2.33	1.42
	Mn	1	1
$\text{Ba}_2\text{Ca}_{0.79}\text{Fe}_{0.5}\text{Nb}_{0.71}\text{O}_{5.35}$	Ba	4.14	4
	Ca	1.50	1.58
	Nb	1.3	1.42
	Fe	1	1
$\text{Ba}_2\text{Ca}_{0.79}\text{Co}_{0.5}\text{Nb}_{0.71}\text{O}_{5.10}$	Ba	4.55	4
	Ca	1.51	1.58
	Nb	2.19	1.42
	Co	1	1

Table S2. The cell parameters of the as-prepared (i) $\text{Ba}_2\text{Ca}_{0.79}\text{Mn}_{0.16}\text{Nb}_{1.05}\text{O}_{5.60}$; (ii) $\text{Ba}_2\text{Ca}_{0.79}\text{Fe}_{0.16}\text{Nb}_{1.05}\text{O}_{5.68}$; (iii) $\text{Ba}_2\text{Ca}_{0.79}\text{Co}_{0.16}\text{Nb}_{1.05}\text{O}_{5.61}$, (iv) $\text{Ba}_2\text{Ca}_{0.67}\text{Mn}_{0.33}\text{NbO}_{5.55}$; (v) $\text{Ba}_2\text{Ca}_{0.67}\text{Fe}_{0.33}\text{NbO}_{5.66}$ and (vi) $\text{Ba}_2\text{Ca}_{0.67}\text{Co}_{0.33}\text{NbO}_{5.53}$ after heat treatment in 5000 ppm $\text{H}_2\text{S}/\text{H}_2$ at 600 °C for 12 h.

Compounds	Cell parameters	
	As-prepared	5000 ppm $\text{H}_2\text{S}/\text{H}_2$ at 600°C
$\text{Ba}_2\text{Ca}_{0.79}\text{Mn}_{0.16}\text{Nb}_{1.05}\text{O}_{5.60}$	8.4135(5) Å	8.420 (1) Å
$\text{Ba}_2\text{Ca}_{0.79}\text{Fe}_{0.16}\text{Nb}_{1.05}\text{O}_{5.68}$	8.4146(2) Å	8.4341(9) Å
$\text{Ba}_2\text{Ca}_{0.79}\text{Co}_{0.16}\text{Nb}_{1.05}\text{O}_{5.61}$	8.4138 (3) Å	8.4231(5) Å
$\text{Ba}_2\text{Ca}_{0.67}\text{Mn}_{0.33}\text{NbO}_{5.55}$	8.3963(7) Å	8.3940(7) Å
$\text{Ba}_2\text{Ca}_{0.67}\text{Fe}_{0.33}\text{NbO}_{5.66}$	8.3750(2) Å	8.3956(8) Å
$\text{Ba}_2\text{Ca}_{0.67}\text{Co}_{0.33}\text{NbO}_{5.53}$	8.3846(3) Å	8.3955(6) Å

Table S3. The EDX analysis of the as-prepared $\text{Ba}_2\text{Ca}_{1-x-y}\text{M}_{x+z}\text{Nb}_{1-z+y}\text{O}_{6-\delta}$ (M = Mn, Fe and Co) after heat treatment in 5000 ppm $\text{H}_2\text{S}/\text{H}_2$ at 600 °C for 12 h.

(i) $\text{Ba}_2\text{Ca}_{0.79}\text{Mn}_{0.16}\text{Nb}_{1.05}\text{O}_{5.60}$; (ii) $\text{Ba}_2\text{Ca}_{0.79}\text{Fe}_{0.16}\text{Nb}_{1.05}\text{O}_{5.68}$; (iii) $\text{Ba}_2\text{Ca}_{0.79}\text{Co}_{0.16}\text{Nb}_{1.05}\text{O}_{5.61}$

M	(i) Mn	(ii) Fe	(iii) Co
S K	0.08	0.42	0.0
Ca K	1.00	1.00	1.00
Ba L	2.98	3.29	2.60
Nb L	1.29	1.45	1.36
M K	0.26	0.52	0.35

(iv) $\text{Ba}_2\text{Ca}_{0.67}\text{Mn}_{0.33}\text{NbO}_{5.55}$; (v) $\text{Ba}_2\text{Ca}_{0.67}\text{Fe}_{0.33}\text{NbO}_{5.66}$; (vi) $\text{Ba}_2\text{Ca}_{0.67}\text{Co}_{0.33}\text{NbO}_{5.53}$

M	(iv) Mn	(v) Fe	(vi) Co
S K	0.00	0.07	0.00
Ca K	1.00	1.00	1.00
Ba L	3.46	2.75	3.68
Nb L	2.05	1.55	1.98
M K	0.36	0.04	0.54