Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for

Substitution of Re^{7+} into $CaMnO_3$: an efficient free electron generation dopant for tuning of thermoelectric properties

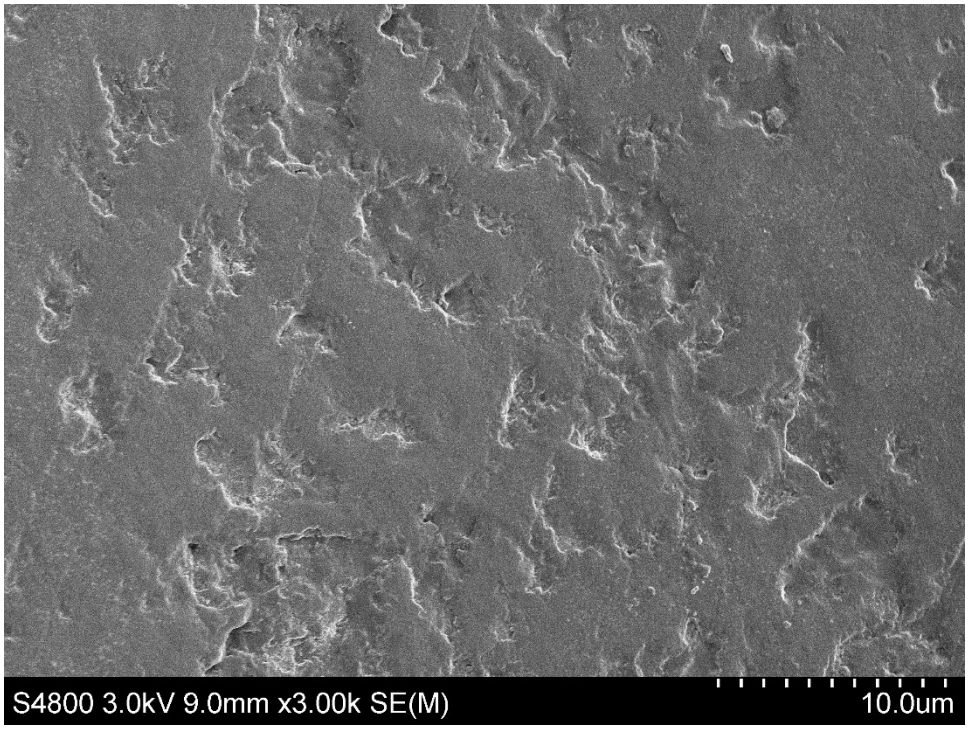
J. Felix Shin,[a] Hongjun Niu,[a] Jonathan Alaria,[b] John B. Claridge,*[a] and Matthew J. Rosseinsky,*[a]

Supplementary Table S1 Relative density and oxygen vacancy content for the $CaMn_{1-x}Re_xO_3$ ($0 \leq x \leq 0.04$).

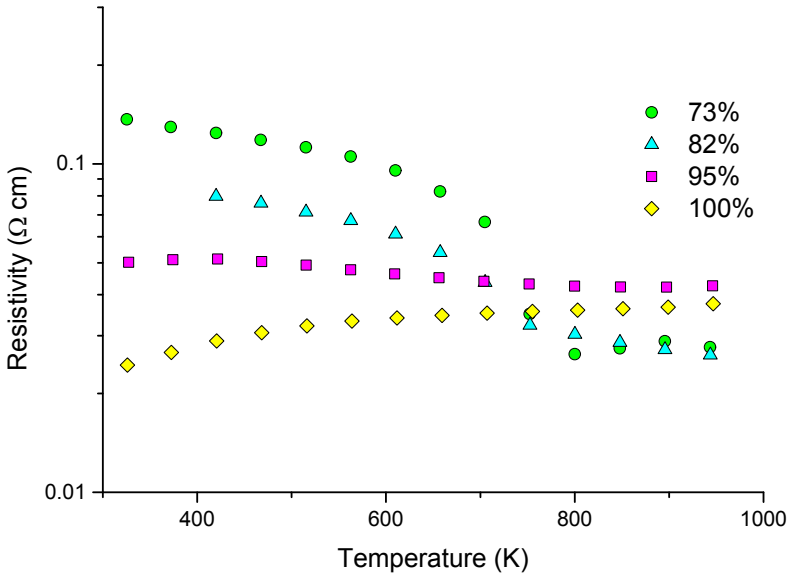
Re content x (nominal)	0	0.005	0.01	0.02	0.03	0.04
Relative density /%	100(1)	99(1)	98(1)	100(1)	98(1)	99(1)
Oxygen vacancy content	0.006(1)	0.005(1)	0.002(1)	0.006(1)	0.005(1)	0.004(1)

Supplementary Table S2 Structural parameters from Rietveld refinement of synchrotron X-ray diffraction data of x = 0.02 at room temperature.

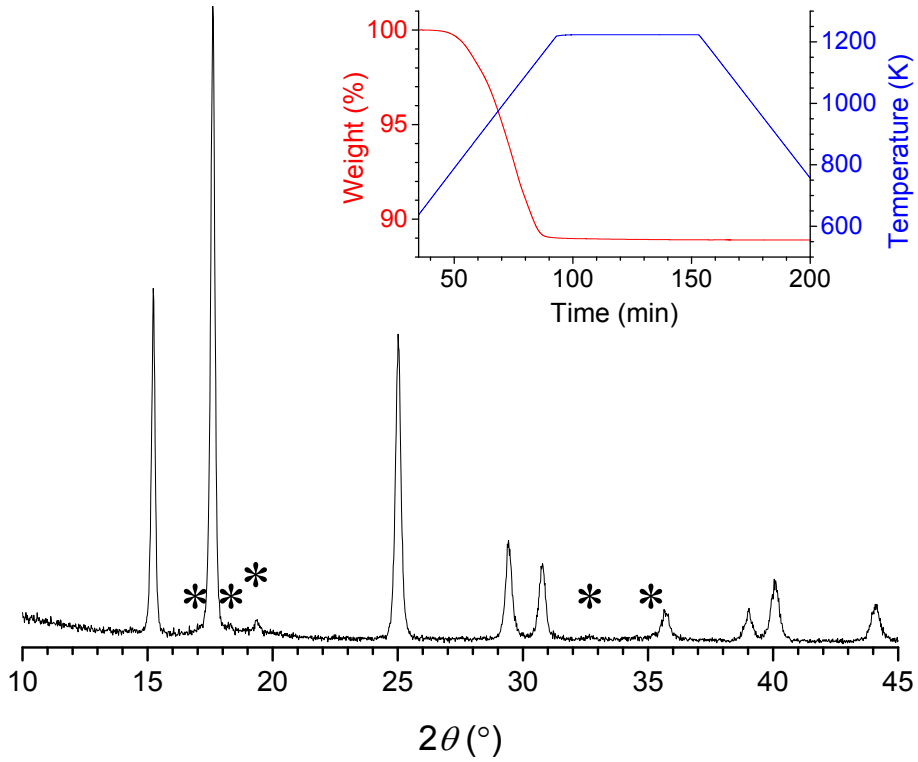
Pnma (62), a = 5.2732(1) Å, b = 7.4650(1) Å, c = 5.2927(1) Å						
atom	multiplicity	x	y	z	occupancy	B_{iso}(Å^2)
Ca	4c	0.0245(2)	0.25	0.0105(4)	1	1.02(5)
Mn	4b	0	0	0.5	0.98	0.52(6)
Re	4b	0	0	0.5	0.02	
O1	4c	0.4835(1)	0.25	0.0116(1)	1	1.35(8)
O2	8d	0.2829(5)	0.0399(3)	-0.2893(4)	1	0.61(8)



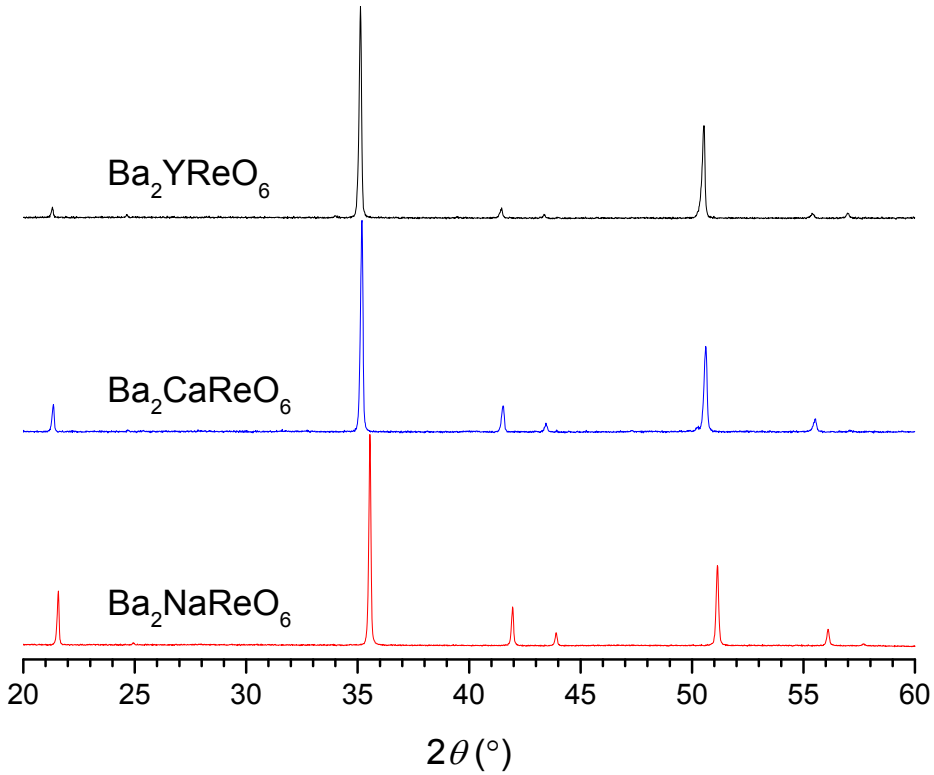
Supplementary Figure S1 Scanning electron micrograph of a sintered x = 0.02. The sample is representative for all the series.



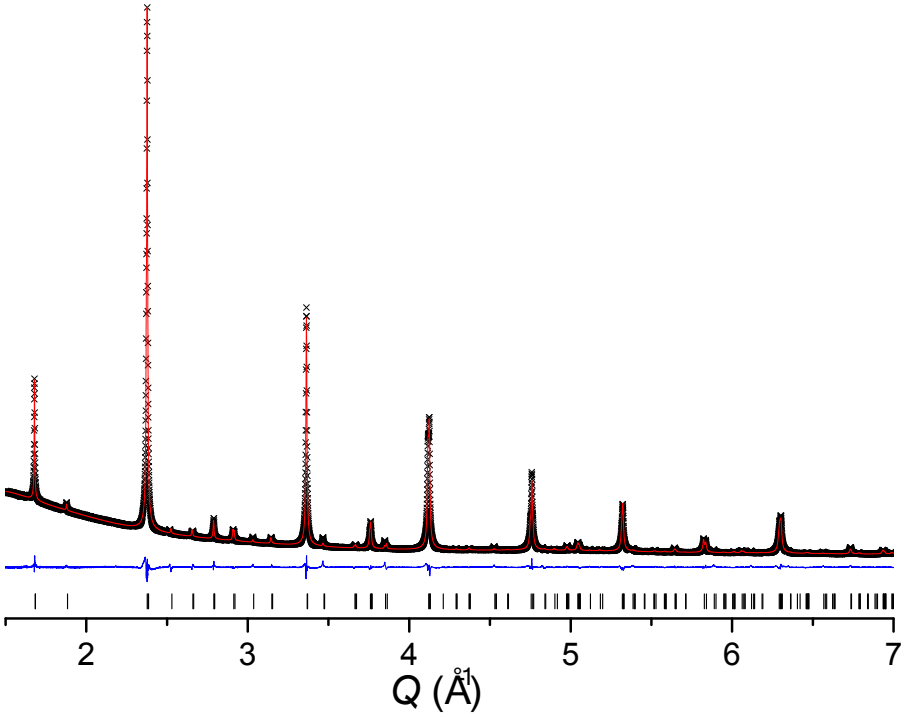
Supplementary Figure S2 Plots of the resistivity as a function of temperature for $CaMnO_3$ with different relative densities of 73(1), 82(1), 95(1) and 100(1)%. Interestingly, the resistivity of the 100(1)% dense undoped $CaMnO_3$ exhibited rather different temperature dependence compared to that of the typical undoped $CaMnO_3$ in literature. Thus, the samples of undoped $CaMnO_3$ with lower relative densities were prepared by varying the sintering temperature. The 73(1)% sample shows the typical behaviour seen in literature: significant decrease in the resistivity with increasing temperature which resembles the behaviour of a semiconductor. The slope, $\Delta\rho/\Delta T$ decreases with increasing relative density and it becomes positive for the 100(1)% sample. This positive $\Delta\rho/\Delta T$ of 100(1)% sample was previously observed for the single crystal studies of $CaMnO_3$ with varying growth condition and rationalised by the high oxygen vacancy content which is disordered.[61] However, the oxygen vacancy content of the single crystal was not given in the paper and that for the 100(1)% sample is 0.006(1) and this is actually less than 0.011(1) of the 73(1)% sample, thus the same explanation cannot be applied here. This variation in the resistivity against the relative density demonstrates the complexity of the electrical properties of the $CaMnO_3$ system and the importance of the relative density for a comparison between the data. The properties of the 100(1)% dense undoped $CaMnO_3$ sample are presented in this paper, since all the properties of the $CaMn_{1-x}Re_xO_3$ ($0 \leq x \leq 0.04$) series are coherent to each other and comparable to other highly dense B-site doped $CaMnO_3$ in literature.[12,29]



Supplementary Figure S3 The thermogravimetric profile of x = 0.02 under flowing 4 vol. % H_2/N_2. A high temperature plateau indicated that the reduction process in this condition was complete (inset) and the laboratory XRD pattern for the reduction product after the thermogravimetric experiment. The peaks in the XRD pattern of the reduction product corresponds to $Ca_{0.5}Mn_{0.5}O$ with a lattice parameter of a_p = 4.6269(3) Å. This phase is isostructural to CaO and MnO but contains Ca and Mn on the same site in 1:1 ratio.[36] For the Re doped samples, additional peaks corresponding to Re metal were identified (marked with *). The most intense *101* reflection was clearly visible at 19.4° along with other weaker peaks.



Supplementary Figure S4 Laboratory XRD patterns for Ba_2YReO_6, Ba_2CaReO_6 and Ba_2NaReO_6. High purity (≥ 99.9%) $BaCO_3$, BaO_2, Y_2O_3, Na_2CO_3, CaO, ReO_2 and Re metal were used. To remove any moisture, Y_2O_3 was preheated in air at 1223 K. The stoichiometric mixtures were ground, pressed into pellets, and sealed in an evacuated silica tube except for the mixture for the Ba_2NaReO_6. The pellets were annealed at 1173–1373 K for 6 h with several intervening regrinding and repelletising steps.



Supplementary Figure S5 Observed (cross), calculated (red), and difference (blue) profiles from Rietveld refinement of synchrotron X-ray diffraction data of x = 0.02 at room temperature. The reliability factors are R_{wp} = 1.94%, R_{exp} = 0.43%, χ^2 = 20.5.