Supplementary Material

Understanding the modulation mechanism of B-site doping CaMnO3-δ thermochemical properties: An Experimental and Computational Study

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Determination of U-values:

We initially determined U_{Mn} = 3.9 eV, U_{Cr} = 3.7 eV, U_{Fe} = 5.3 eV based on the computational parameters available in the Materials Project database. The same U values were taken in the paper [44] by Amit Mishra et al. for the CaMnO3 system material. Their calculations show that this U-value taken allows the calculations to be closer to the experimental values. Meanwhile, we carried out the linear response method to determine the U values as U_{Mn} = 6.3 eV, U_{Cr} = 4.0 eV, and U_{Fe} = 5.7 eV. Subsequently, we recalculated all the different U values and found that the optimized cell parameters obtained by the linear response method deviated more from the experimental values, so we finally chose the original scheme.

Table S1 Calculated values of lattice constant a(Å) for different U values

Sample name	experimental a(Å)	Calculated a(Å) when U_{Mn} = 3.9 eV, U_{Cr} = 3.7 eV, U_{Fe} = 5.3 eV	Calculated a(Å) when U_{Mn} = 6.3 eV, U_{Cr} = 4.0 eV, U_{Fe} = 5.7 eV
CM	3.788	3.792	3.834
CMC12.5	NA	3.802	3.835
CMF12.5	3.797	3.803	3.835

The TG curves of Cr-doped $CaMnO_3$ and Fe-doped $CaMnO_3$ samples are shown in **Fig. 2a** and **Fig. 2c**. The corresponding thermal storage characteristic parameters can be calculated from the thermogravimetric experimental data, where Δm is the mass change during the

reaction. The information calculated from the thermogravimetric data is shown in **Tables S2 and S3**.

Table S2 Reaction performance of Cr-doped $CaMnO_3$

Sample name	T_{start}	Δm_{re}	Δm_{ox}	α_{cyc}
CM	690℃	1.68%	1.48 %	88.10 %
CMC12.5	680℃	2.39%	2.31%	96.71%
CMC25	680℃	2.34%	2.30%	98.56 %

Table S3 Reaction performance of Fe-doped $CaMnO_3$

Sample name	T_{start}	Δm_{re}	Δm_{ox}	α_{cyc}
CM	690℃	1.68 %	1.48 %	88.10 %
CMF6.25	624℃	2.83 %	2.38 %	84.10 %
CMF12.5	591℃	2.54 %	2.50 %	98.43 %
CMF18.75	430℃	2.30 %	2.20 %	95.65 %
CMF25	400℃	2.20 %	2.09 %	95.00 %

The meaning of each parameter in the table is as follows:

T_{start}- reduction onset temperature, the temperature at which the sample begins to lose weight in the second cycle;

Δm_{re}- reduction reactivity, the difference of mass between the initial equilibrium and the maximum weight loss in the second cycle.

Δm_{ox}- reoxidation reactivity, the difference of mass between the maximum weight loss and the reoxidation reaction equilibrium in the second cycle.

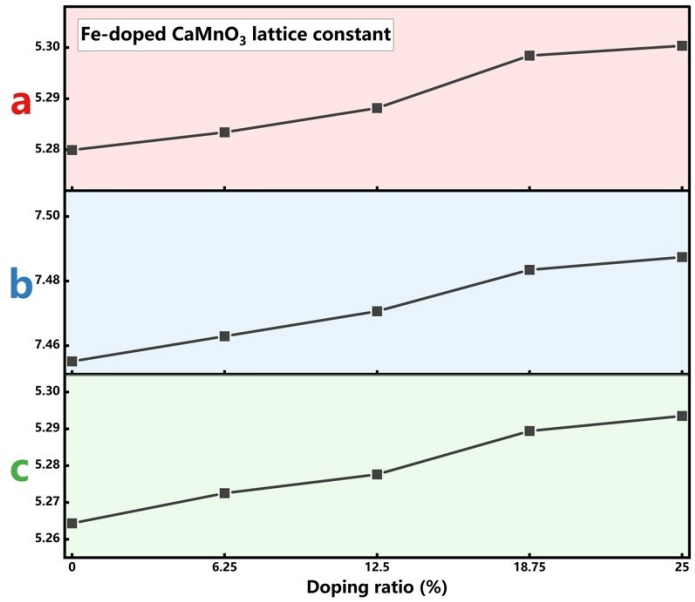
α_{cyc}- Reversible reaction rate，$\alpha_{cyc}=\Delta m_{ox}/\Delta m_{re}$；

Table S4 lists the experimental lattice constants obtained from Rietveld refinement and the optimized lattice constants from DFT calculations. These include the tetragonal phase at room temperature and the cubic phase at high temperature. It can be observed that the difference between the experimental and calculated values is very small.

Table S4 Experimental and calculated values of lattice constant a(Å)

Sample name	a(Å) of quadratic phase	a(Å) of cubic phase	Calculated value of a(Å) (cubic)	Difference
CM	5.280	3.788	3.792	0.1%
CMC12.5	5.285	NA	3.802	NA
CMF12.5	5.288	3.797	3.803	0.2%

Rietveld refinement was used to analyze XRD results of Fe-doped CaMnO3, producing three lattice constant curves shown in **Fig. S1**.



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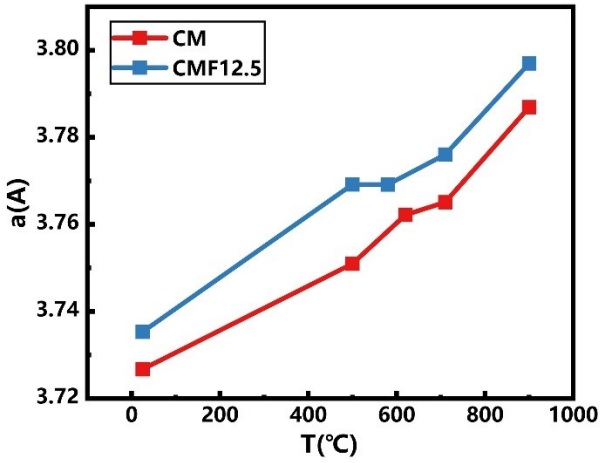
48 **Fig. S1** The lattice constant of Fe-doped $CaMnO_3$

49 Rietveld refinement was performed on the in situ XRD test results of CM and CMF12.5 to

50 obtain lattice constant versus temperature curves, as illustrated in **Fig. S2**.



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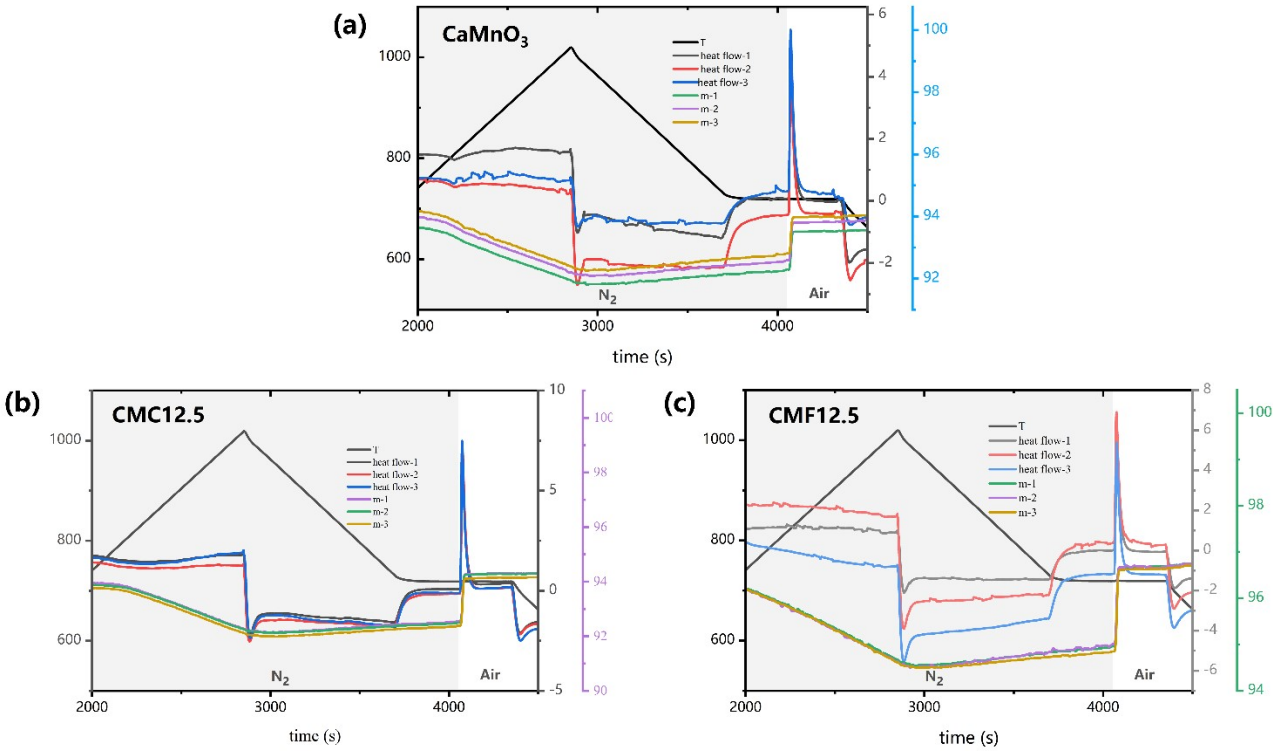
52 **Fig. S2** The lattice constant of CM and CMF12.5 changes with temperature



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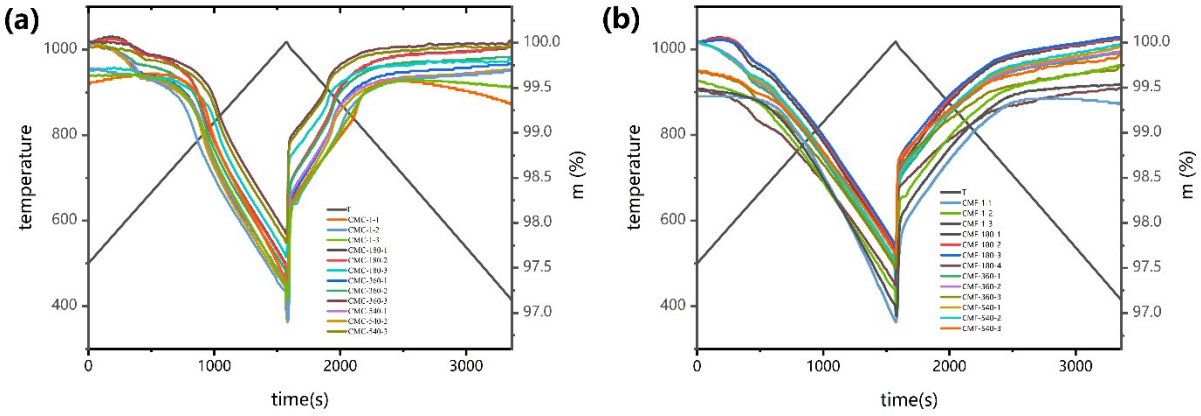
54 **Fig. S3** The TG-DSC performance: (a) CM; (b) CMC12.5; (c) CMF12.5



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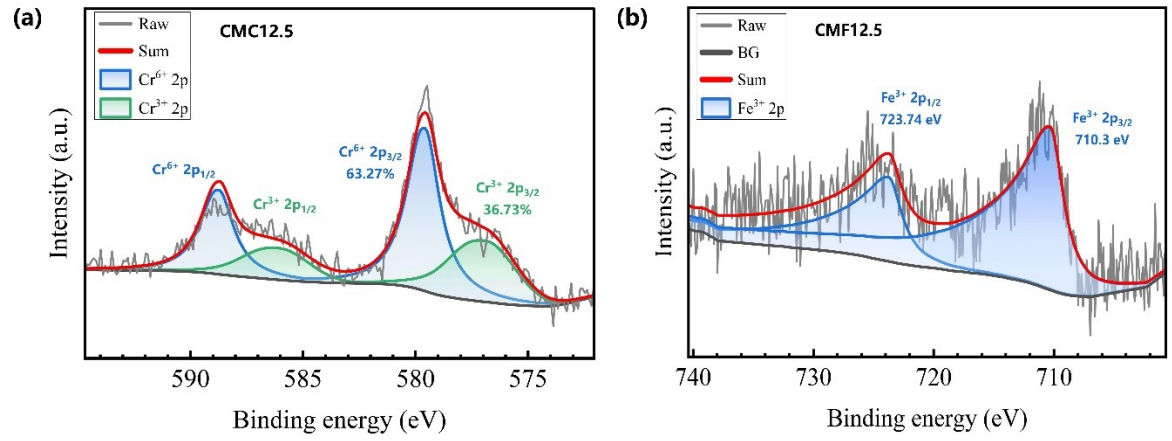
56 **Fig. S4** The cycling performance: (a) CMC12.5; (b) CMF12.5



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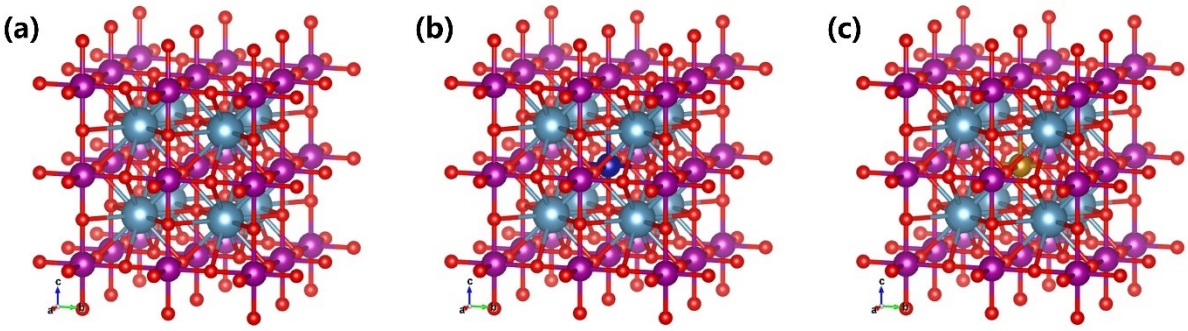
58 **Fig. S5** XPS spectra analysis: (a) Cr2p XPS spectra peak results of CMC12.5; (b) Fe2p XPS

59 spectra peak results of CMF12.5



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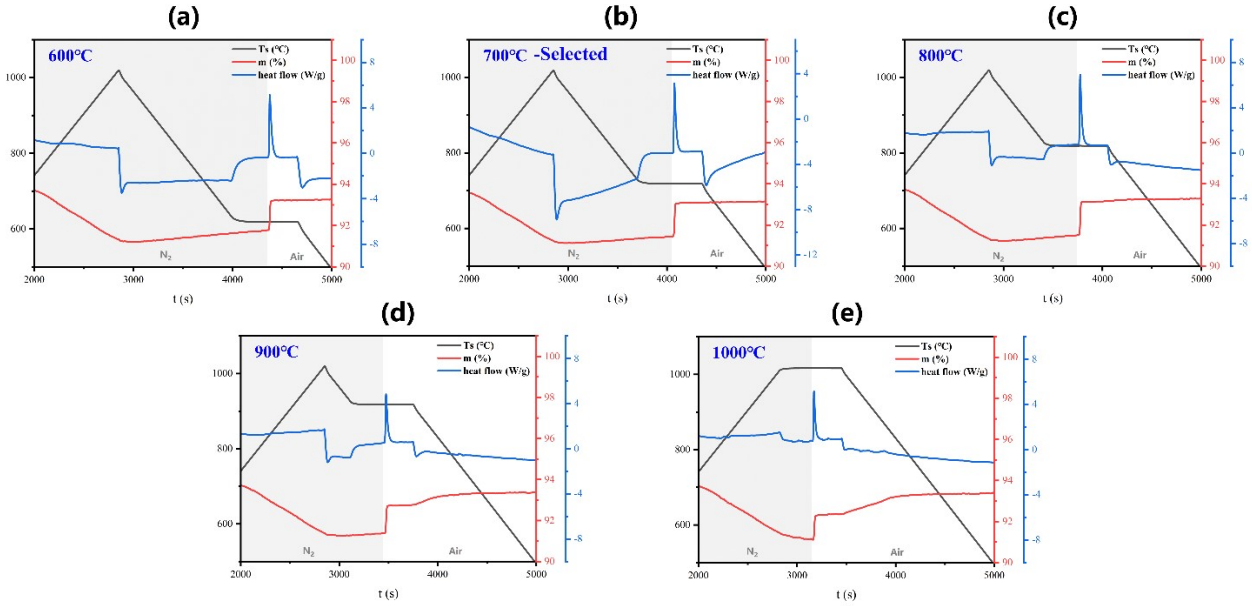
61 **Fig. S6** VASP simulation calculation models: (a) CM; (b) CMC12.5; (c) CMF12.5.



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63 **Fig. S7** Comparison and selection of DSC test solutions.