

Supporting Information

Effect of nitrogen substitution on the structural and magnetic ordering transitions of NiCr_2O_4

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KEYWORDS: NiCr_2O_4 ; ammonolysis; phase transition; magnetic property; heat capacity

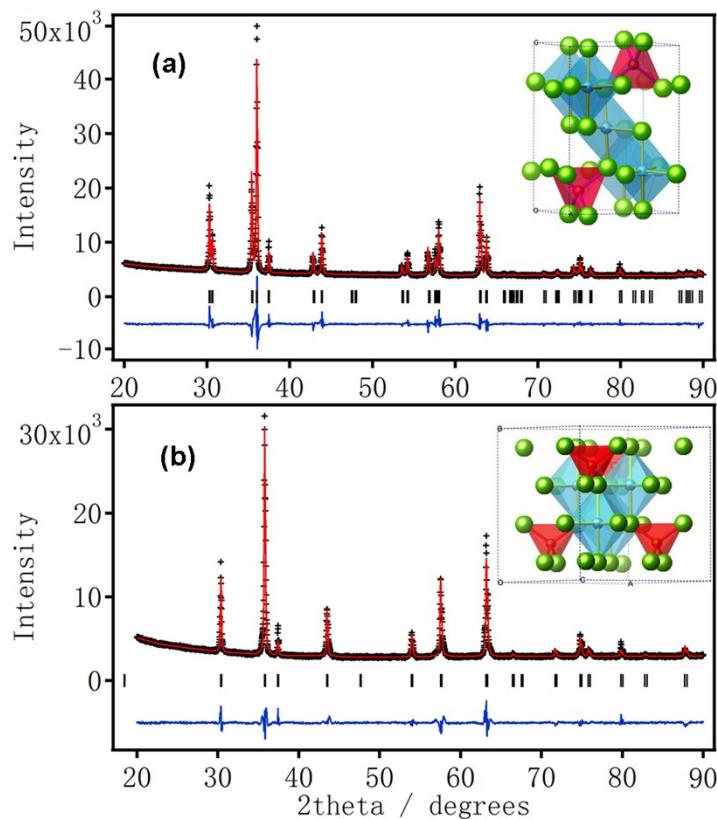


Figure S1. Rietveld refinements of NiCr_2O_4 (a) and N600 (b) : T - tetrahedral and C - cubic.

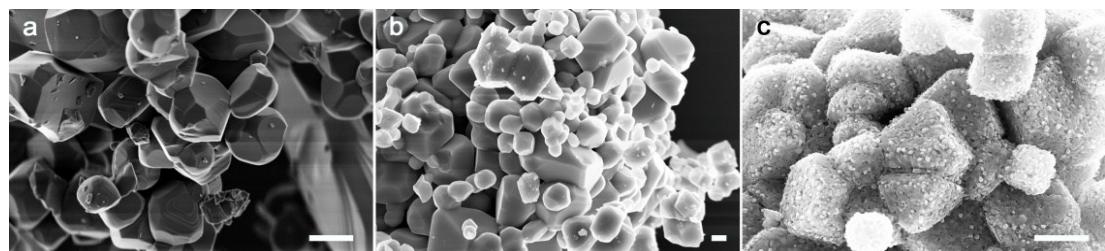


Figure S2. SEM images of NiCr_2O_4 (a), N500(b) and N600(c): scale bars are 1 μm .

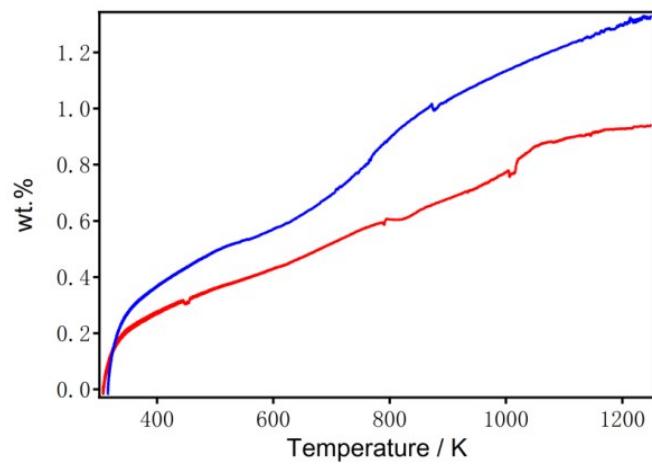


Figure S3. TG results of N500(red) and N600(blue).

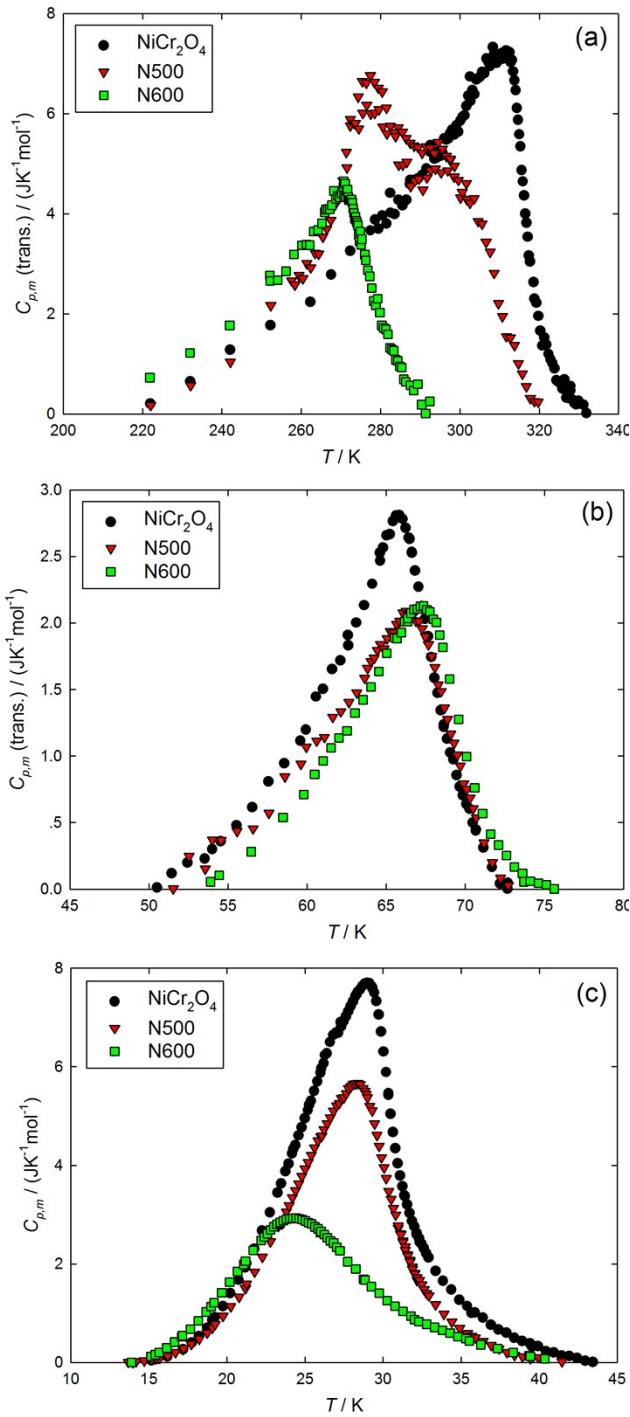


Figure S4. Plot of magnetic or structural heat capacities of NiCr_2O_4 , $\text{NiCr}_2\text{O}_{3.68}\text{N}_{0.213}$ (N500) and $\text{NiCr}_2\text{O}_{3.55}\text{N}_{0.300}$ (N600) obtained by subtracting the lattice heat capacities from the total heat capacities in the first (a), the second (b) and the third (c) transition temperature region.

Table S1: Fitting parameters of the Debye and Einstein functions used in the lattice heat capacity estimation.

Parameters	NiCr ₂ O ₄	N500	N600
<i>m</i> /mole	0.91	0.88	0.61
Θ_D /K	129.44	126.20	96.12
<i>n</i> ₁ /mole	4.46	4.24	4.37
$\Theta_{E,1}$ /K	666.64	696.03	643.43
<i>n</i> ₂ /mole	1.61	1.83	1.75
$\Theta_{E,2}$ /K	277.27	293.31	238.13
%RMS	1.53	2.04	2.08

Table S2: Transition starting, ending and peak temperatures and entropy changes of NiCr₂O₄, N500 and N600 in the corresponding transition temperature regions.

	Samples	NiCr ₂ O ₄	N500	N600
First Transition	T _s /K	218.5	219	217
	T _e /K	332	320	293
	T _p /K	308-312	277-295	270.5
	ΔS/(JK ⁻¹ mol ⁻¹)	1.14	1.05	0.59
Second Transition	T _s /K	50	51.5	53.5
	T _e /K	73	73	75.6
	T _p /K	65.7	66.3	67.2
	ΔS/(JK ⁻¹ mol ⁻¹)	0.39	0.32	0.30
Third Transition	T _s /K	15	13.5	14
	T _e /K	43	41.5	41
	T _p /K	29	28.2	24.3
	ΔS/(JK ⁻¹ mol ⁻¹)	2.53	1.85	1.30

Table S3: Fitting parameters of heat capacities of NiCr₂O₄ and N-doped samples below 10 K.

Parameters	NiCr ₂ O ₄	N500	N600
$\gamma/(J \cdot K^{-2} \cdot mol^{-1})$	1.72819E-03	2.27941E-03	2.42508E-03
$B_3/(J \cdot K^{-4} \cdot mol^{-1})$	1.08250E-03	1.17849E-03	1.98657E-03
$B_5/(J \cdot K^{-6} \cdot mol^{-1})$	-1.72950E-05	-2.11485E-05	-2.50273E-05
$B_7/(J \cdot K^{-8} \cdot mol^{-1})$	2.00284E-08	3.57341E-08	4.70507E-08
$B_{asw}/(J \cdot K^{-4} \cdot mol^{-1})$	1.05542E-02	9.55453E-03	9.92431E-03
$A/(K)$	21.71	19.14	20.43
%RMS	0.90	0.67	0.66