Supplementary Material

Fundamental material property trends in the $La_{0.8-x}Nd_xCa_{0.2}FeO_{3-\delta}$ series: crystal structure and thermal expansion

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1. Material characterisation

1.1 Quantitative phase analysis

Formation of secondary phases (CaO and $Ca_2Fe_2O_5$) were caused by substitution with high concentrations of Nd (x≥0.7 for $La_{0.8-x}Nd_xCa_{0.2}FeO_{3-\delta}$). Table S-1 gives the results of the XRD quantitative phase analysis for $La_{0.1}Nd_{0.7}Ca_{0.2}FeO_{3-\delta}$.

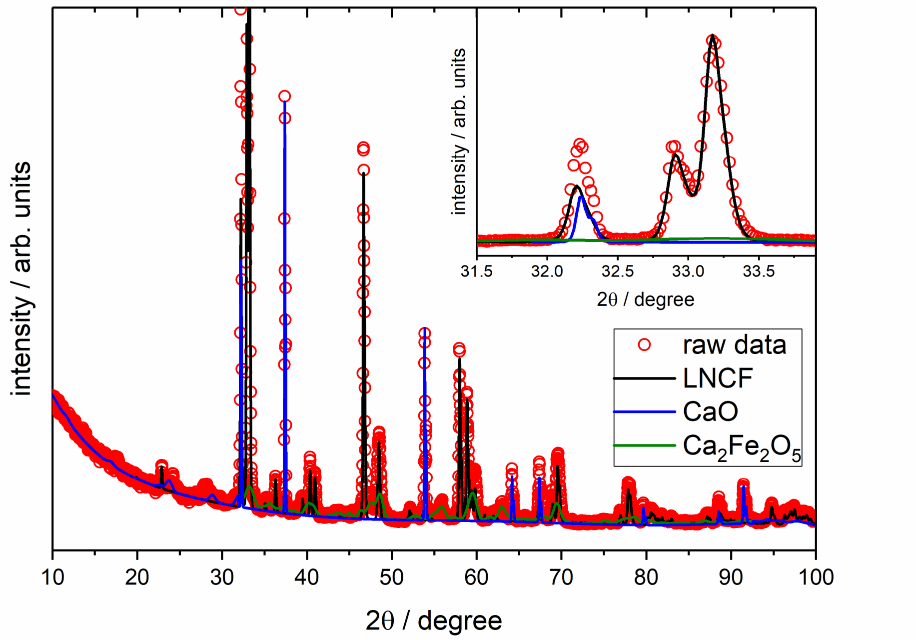


Fig. S-1. Room temperature powder diffraction pattern of $La_{0.1}Nd_{0.7}Ca_{0.2}FeO_{3-\delta}$ (LNCF) (circles) and fit obtained from Rietveld refinement (solid lines represent the refined patterns of CaO and $Ca_2Fe_2O_5$; quantitative analysis in Table S-1).

Tab. S-1. Weight percent fraction of the $La_{0.1}Nd_{0.7}Ca_{0.2}FeO_{3-\delta}$ phase mixture calcined at 1200°C for 10 h.

compound	**wt-%**
$La_{0.8-x}Nd_xCa_{0.2}FeO_{3-\delta}$ *	66
CaO	26
$Ca_2Fe_2O_5$	8

*matrix with unknown cation composition.

1.2 Thermal expansion and phase transition

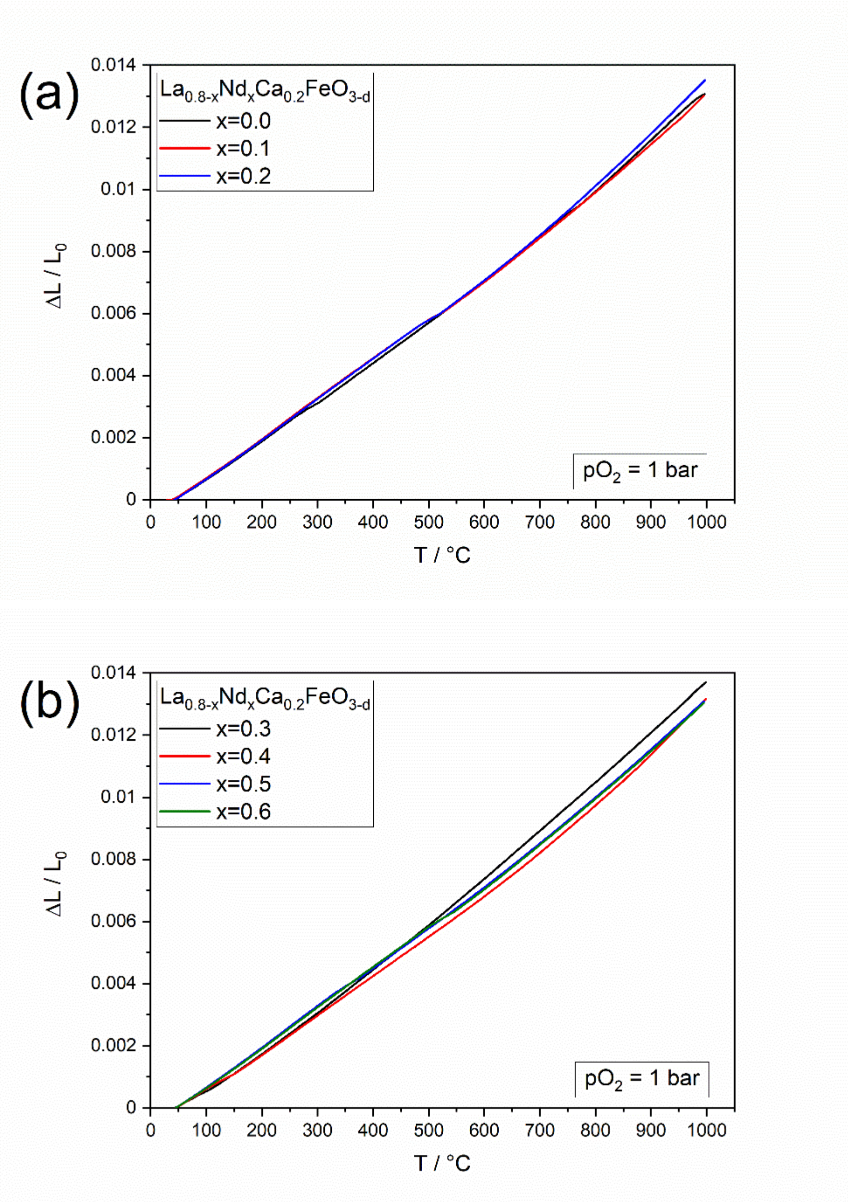
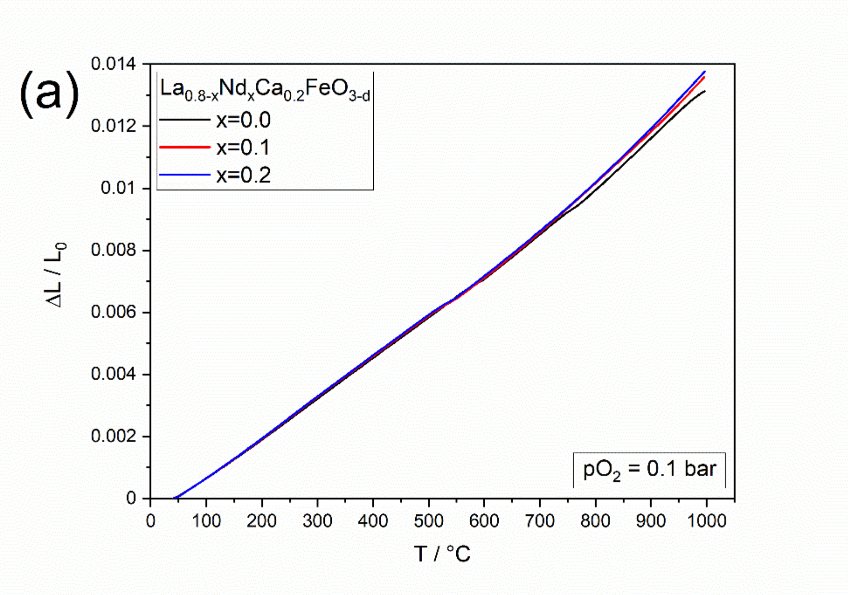


Fig. S-2. Thermal expansion of dense ceramic samples from the series $La_{0.8-x}Nd_xCa_{0.2}FeO_{3-\delta}$ ($0 \leq x \leq 0.6$) for (a) x=0-0.2 and (b) x=0.3-0.6 at pO_2 = 1 bar. The expansion curve of $La_{0.8}Ca_{0.2}FeO_{3-\delta}$ (x=0) was taken from [1].



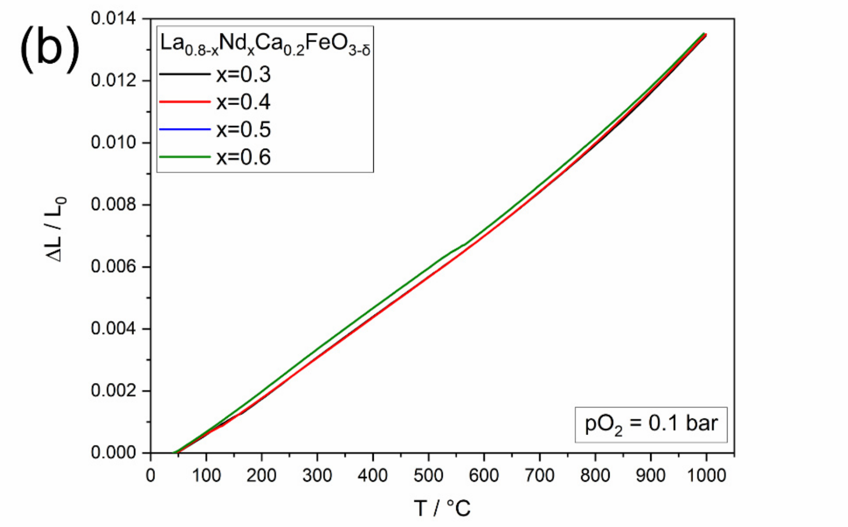


Fig. S-3. Thermal expansion of dense ceramic samples from the series $La_{0.8-x}Nd_xCa_{0.2}FeO_{3-\delta}$ ($0 \leq x \leq 0.6$) for (a) x=0-0.2 and (b) x=0.3-0.6 (expansion curves for x=0.3 and x=0.5 superimpose with those of x=0.4) at pO_2 = 0.1 bar. The expansion curve of $La_{0.8}Ca_{0.2}FeO_{3-\delta}$ (x=0) was taken from [1].

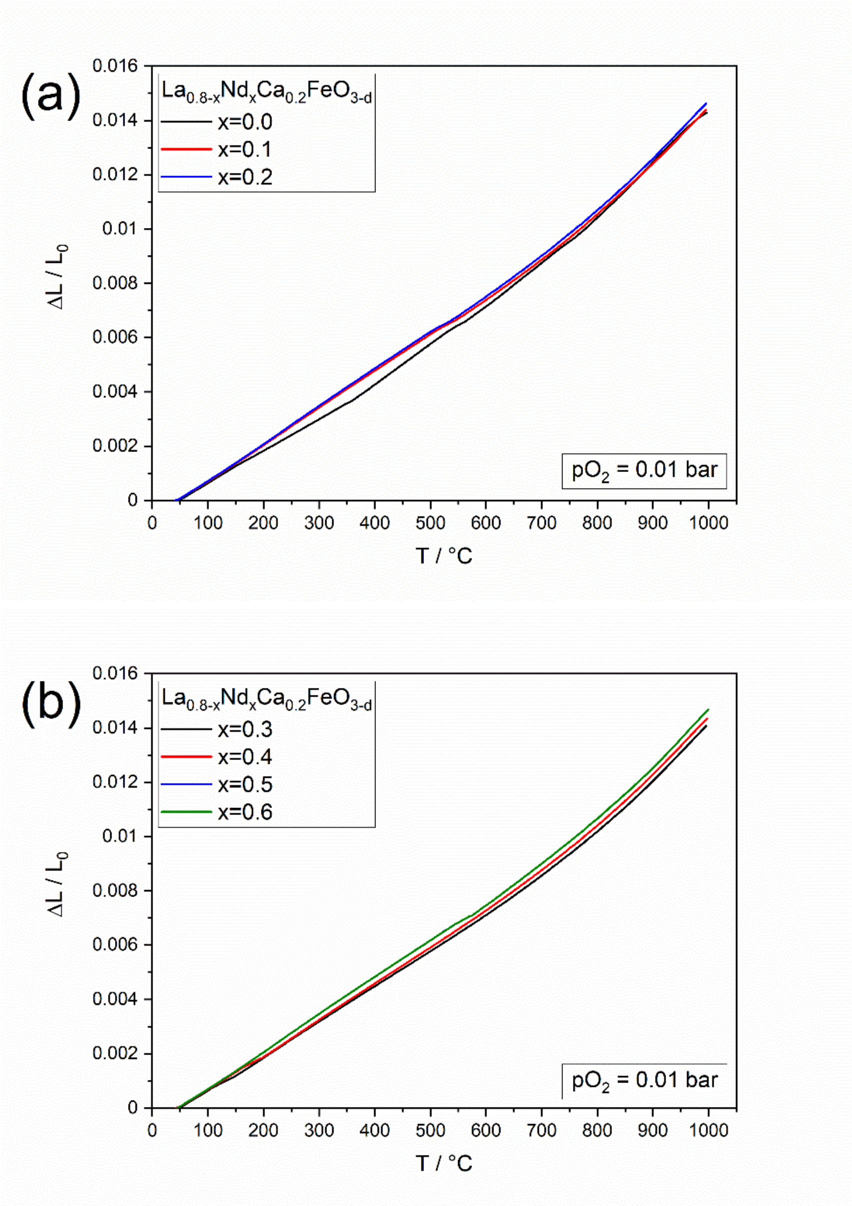


Fig. S-4. Thermal expansion of dense ceramic samples from the series $La_{0.8-x}Nd_xCa_{0.2}FeO_{3-\delta}$ ($0 \leq x \leq 0.6$) for (a) x=0-0.2 and (b) x=0.3-0.6 (expansion curve for x=0.5 superimpose with those of x=0.3) at pO_2 = 0.01 bar. The expansion curve of $La_{0.8}Ca_{0.2}FeO_{3-\delta}$ (x=0) was taken from [1].

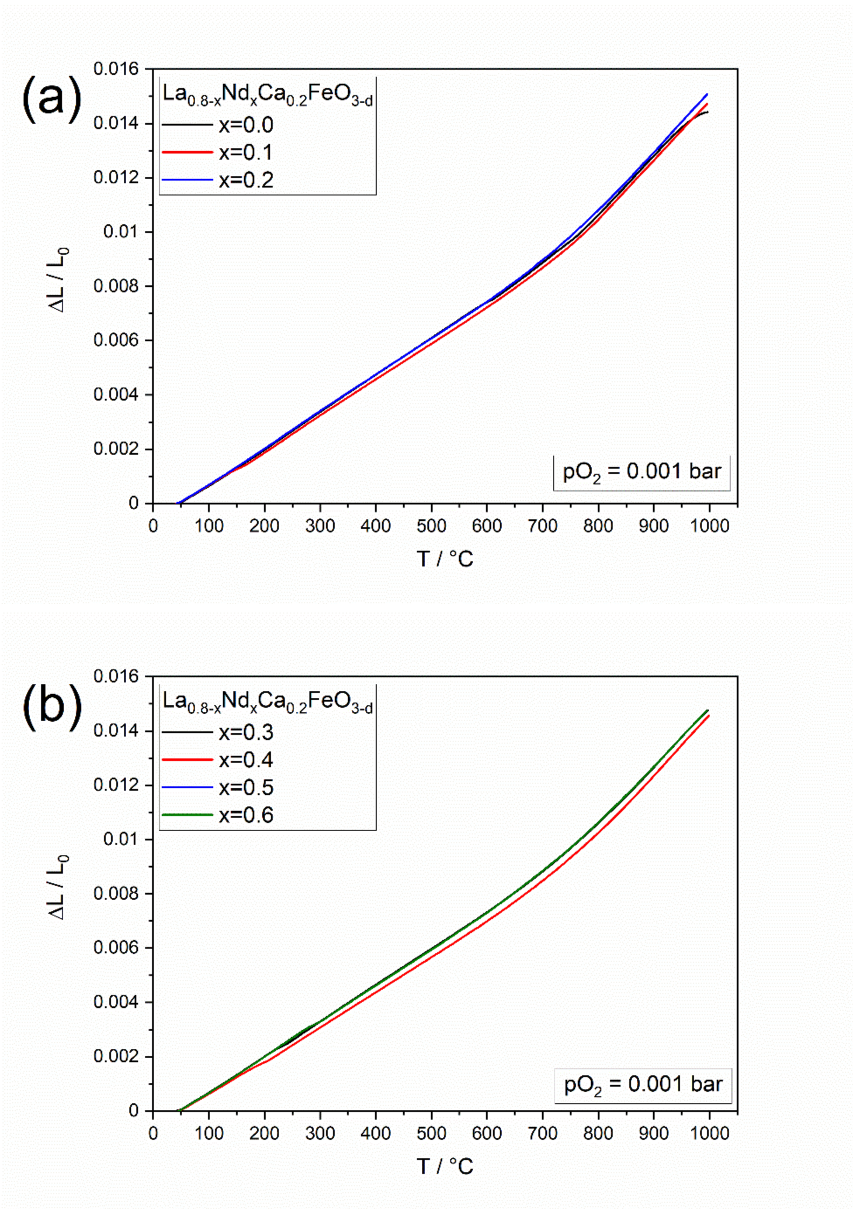


Fig. S-5. Thermal expansion of dense ceramic samples from the series $La_{0.8-x}Nd_xCa_{0.2}FeO_{3-\delta}$ ($0\leq x\leq 0.6$) for (a) x=0-0.2 and (b) x=0.3-0.6 (expansion curves for x=0.3 and x=0.5 superimpose with those of x=0.6) at pO_2 = 0.001 bar. The expansion curve of $La_{0.8}Ca_{0.2}FeO_{3-\delta}$ (x=0) was taken from [1].

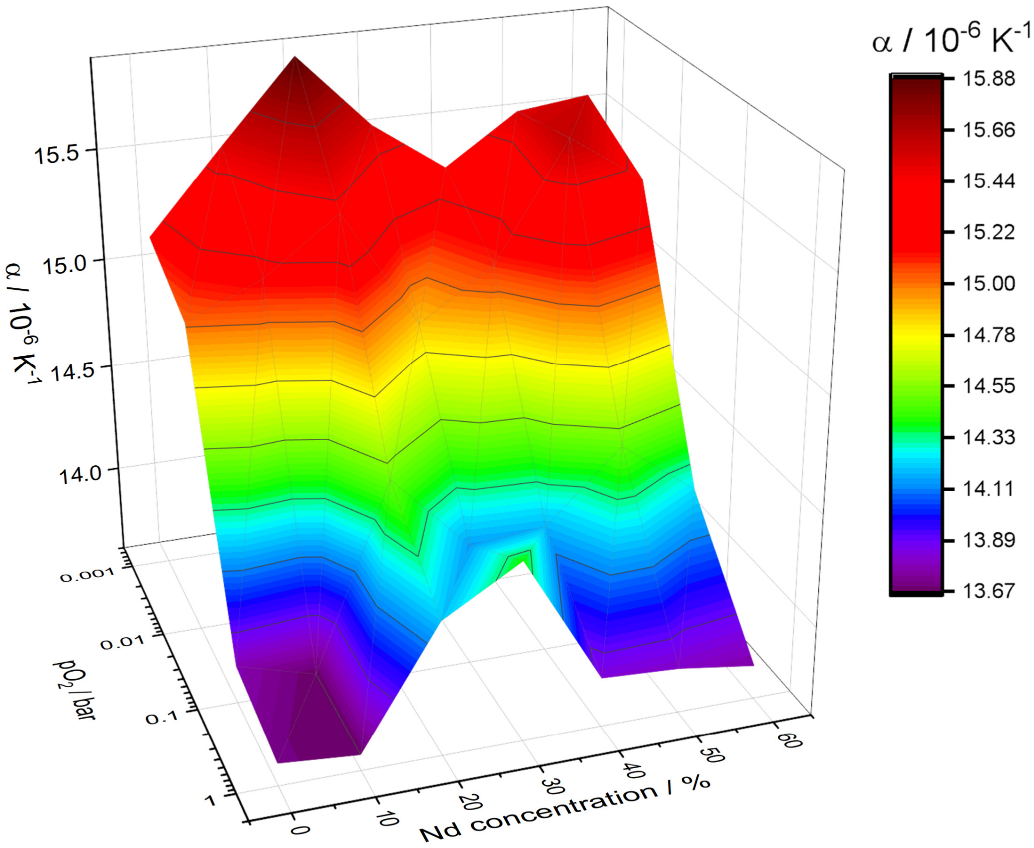


Fig. S-6. Average thermal expansion coefficients of $La_{0.8-x}Nd_xCa_{0.2}FeO_{3-\delta}$ ($0 \leq x \leq 0.6$) in the temperature range $50 \leq T/°C \leq 1000$ as a function of Nd concentration and oxygen partial pressure; data for the Nd-free compound was taken from literature [1].

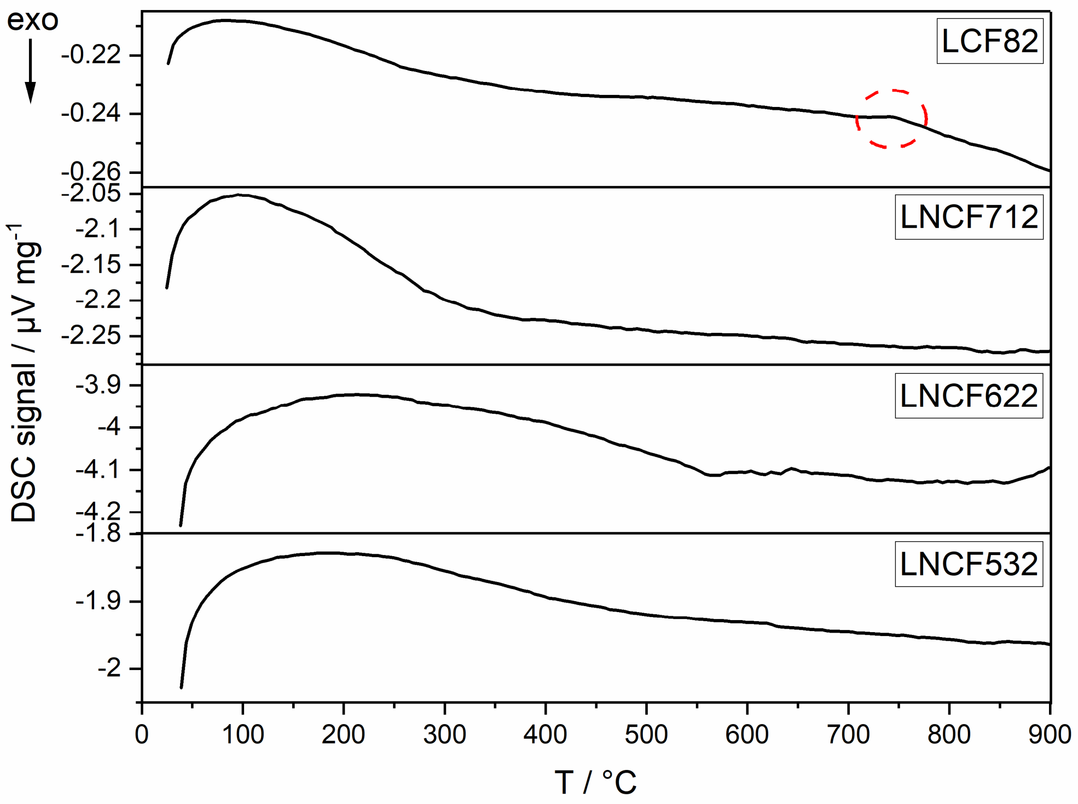


Fig. S-7. Differential scanning calorimetry (DSC) of $La_{0.8-x}Nd_xCa_{0.2}FeO_{3-\delta}$ (LCF82), $La_{0.7}Nd_{0.1}Ca_{0.2}FeO_{3-\delta}$ (LNCF712), $La_{0.6}Nd_{0.2}Ca_{0.2}FeO_{3-\delta}$ (LNCF622) and $La_{0.5}Nd_{0.3}Ca_{0.2}FeO_{3-\delta}$ (LNCF532) in 20% O_2-rest Ar; The peak at approximately 740°C (for LCF82; dashed circle) is due to the reversible phase transformation from the orthorhombic to the trigonal modification, which was also reported by Price *et al.* [2]. In contrast, no peaks were observed for the Nd-containing compounds.

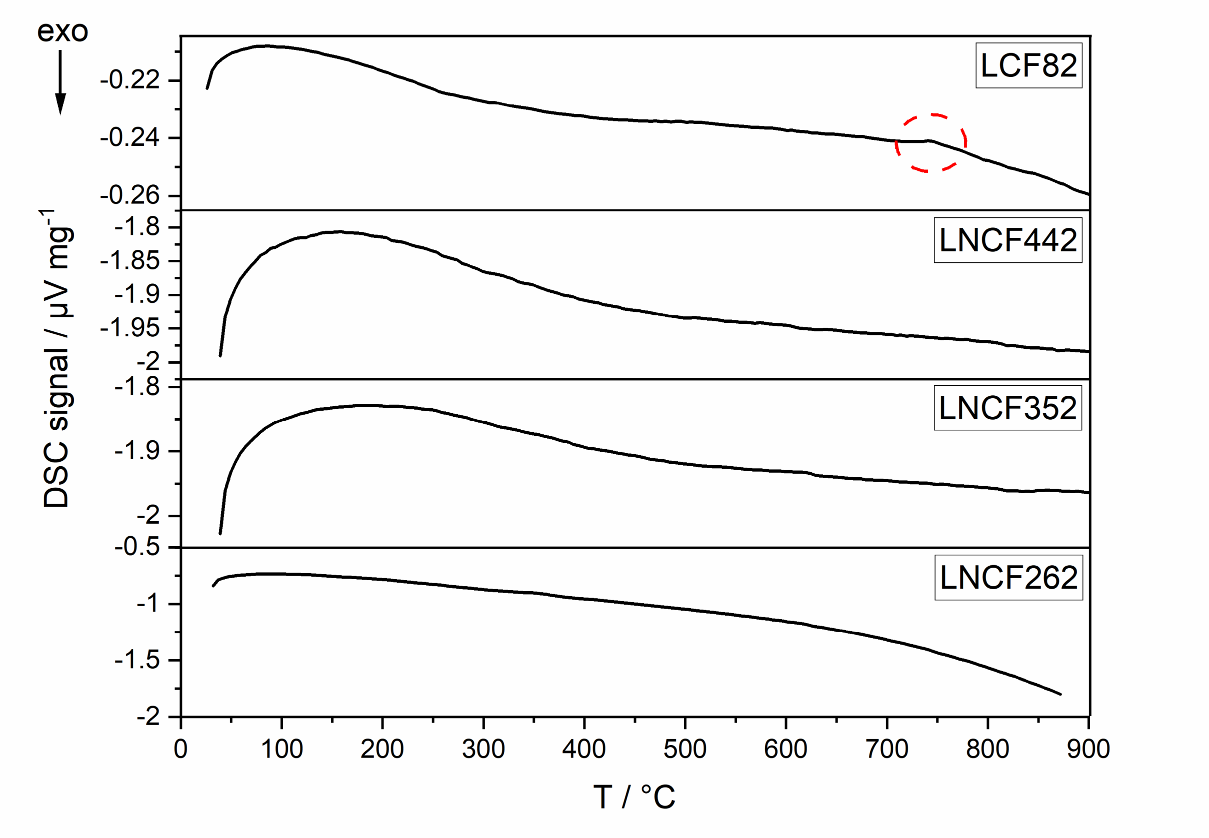


Fig. S-8. DSC of $La_{0.8-x}Nd_xCa_{0.2}FeO_{3-\delta}$ (LCF82), $La_{0.4}Nd_{0.4}Ca_{0.2}FeO_{3-\delta}$ (LNCF442), $La_{0.3}Nd_{0.5}Ca_{0.2}FeO_{3-\delta}$ (LNCF352) and $La_{0.2}Nd_{0.6}Ca_{0.2}FeO_{3-\delta}$ (LNCF262) in 20% O_2-rest Ar; The peak at approximately 740°C (for LCF82; dashed circle) is due to the reversible phase transformation from the orthorhombic to the trigonal modification, which was also reported by Price *et al.* [2]. In contrast, no peaks were observed for the Nd-containing compounds.

2. References

[1] Berger C, Bucher E, Windischbacher A, Boese AD, Sitte W (2018) Strontium-free rare earth perovskite ferrites with fast oxygen exchange kinetics: Experiment and theory. J Solid State Chem 259:57-66. doi:10.1016/j.jssc.2017.12.019

[2] Price PM, Rabenberg E, Thomsen D, Misture ST, Butt DP (2014) Phase transformations in calcium-substituted lanthanum ferrite. Journal of the American Ceramic Society 97 (7):2241-2248. doi:10.1111/jace.12891