Electronic Supplementary Material (ESI) for Nanoscale.

Supplemental Information

Details of STEM EDX Mapping

STEM EDX elemental mapping as described in the main text revealed that the brightest phase (GdFeCeCo or GFCC phase) contained Gd,Ce,Co and Fe with relative element ratios as shown in Table 1S. The Fe/Co ratio was reduced to ~1.87 from 2 in the CFO phase, while the Gd/Ce ratio was reduced from 0.25 to 0.14 in the GDC phase. The SAED for each of the phases were collected as shown in Fig. S1a-c.

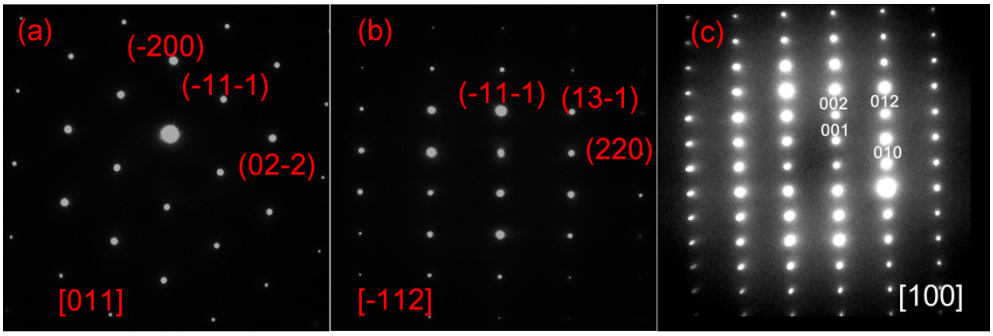

Figure S1. SAED patterns for (a) GDC, (b) CFO, and (c) GFCC regions as identified using STEM EDX in Fig. 2.

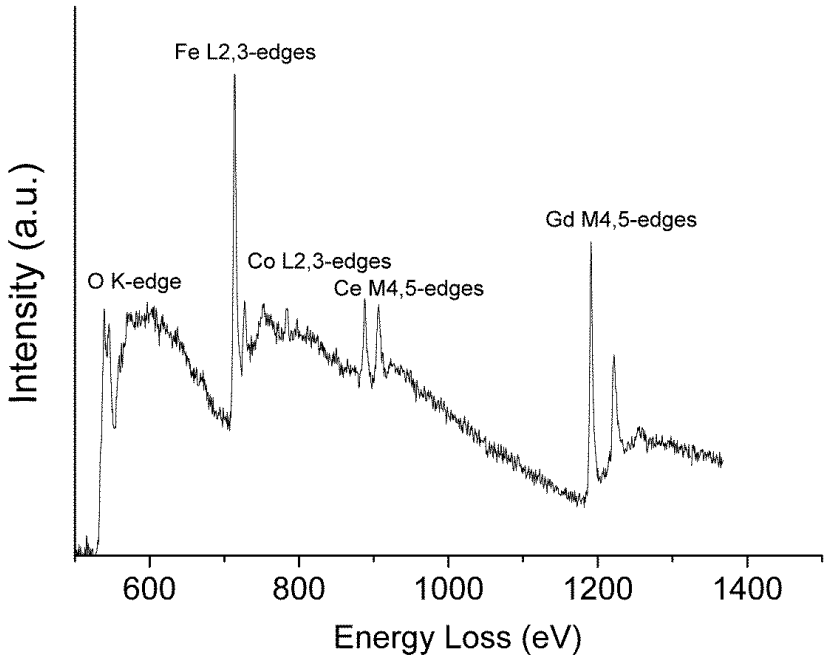

Fig. S2 EELS scan taken from inside the GFCC phase.

The CFO and GDC retain the spinel and fluorite structure after the membrane fabrication procedure, exhibiting a cubic structure with space group of F d -3 m (227) and F m -3 m (225) respectively. The SAED were well indexed and matched with the ICSD related phases as mentioned for the starting powders. The formation of the new GFCC phase showed a large d-spacing of 0.81nm (001) with a double layered structure.

The atomic element ratio from different grains of the GDC, CFO and GFCC phases are summarized in Table 1S. Considering the structural and chemical information obtained from these detailed TEM investigations, the following reactions are proposed to occur during sintering of the GDC and CFO nanocrystalline starting materials into membrane composites at 1300 °C.

$$Gd_{0.2}Ce_{0.8}O_{1.85} + CoFe_2O_4 + Co_{1.09}Fe_{1.81}O_4 \rightarrow Gd_{0.374}Ce_{0.079}Co_{0.077}Fe_{0.47}O_x + Co_{1.05}Fe_{2.00}O_4 + Gd_{0.16}Ce_{0.84}O_{2-\delta}$$

The degree of oxygen non-stoichiometry together with the atomic structure of the third GFCC phase is a subject of current work using Electron Energy Loss Spectroscopy (EELS).

Table 1S: Atomic element ratio from different grains as pointed in Fig. 2 and relative ratios of B site elements to A site elements.

	Gd	Ce	Co	Fe	Fe/Co	Gd/Ce	Gd/Fe	(Ce+Co)/(Gd+Fe+Ce+Co)	(Gd+Ce)/(Co+Fe)
GFCC	37.40	7.90	7.70	47.00	6.11	4.82	0.80	15.6	0.83
CFO	-	-	34.50	65.50	1.90				
GDC	15.70	84.30	-	-		0.19			