

Hydrothermal Synthesis, Characterization, and Sintering Behavior of Core-Shell Particles: A Principle Study on Lanthanum Strontium Cobaltite Coated with Nanosized Gadolinium Doped Ceria

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Supplementary Material

1. Details on the commercial $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.99}\text{CoO}_3$ powder used as the core material

According to the information from the provider (Kusaka Rare Metal Products), the commercial $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.99}\text{CoO}_3$ (LSC) powders were produced by the organic acid complex method in following steps (refer to <http://www.kusaka.co.jp/works/chemicals/oxides/>): (1) dissolve or disperse the metal carbonates or metal hydroxides in water, (2) form precursors by adding organic acids, for instance, citric acid, malic acid etc., (3) dry and calcine the precursors, (4) mill the products into powders of a desired size. Before preparing core-shell particles, the laser diffraction measurement was used to analyze the particle size distribution of the as-obtained commercial LSC powders. The result is presented in **Figure S1**. The quantification range was from 0.04 μm to 2000 μm , and D10, D50 and D90 were 0.178 μm , 0.388 μm and 1.255 μm respectively.

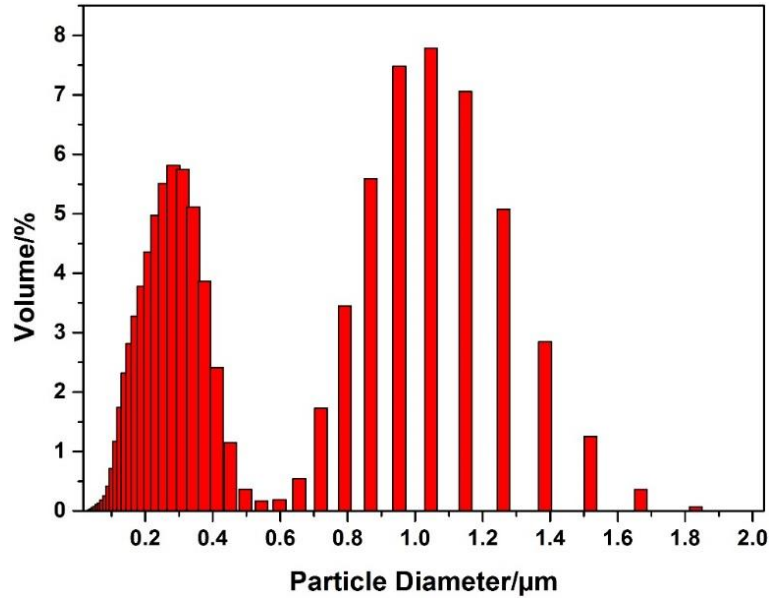


Figure S1. Particle size distribution of the commercial $(La_{0.6}Sr_{0.4})_{0.99}CoO_3$ powder

2. Details on the densification process by spark plasma sintering and by conventional sintering

Profiles of the spark plasma sintering process are presented in **Figure S2**. The electric current, the temperature, the applied pressure and the displacement were recorded simultaneously during the sintering process. The programmed temperature profile during the conventional sintering in a muffle furnace is presented in **Figure S3**.

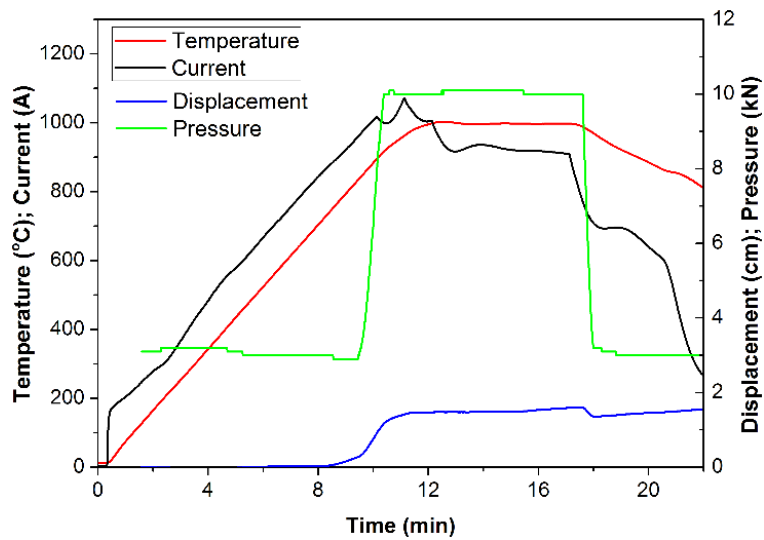


Figure S2. Profiles of the spark plasma sintering of core-shell particles

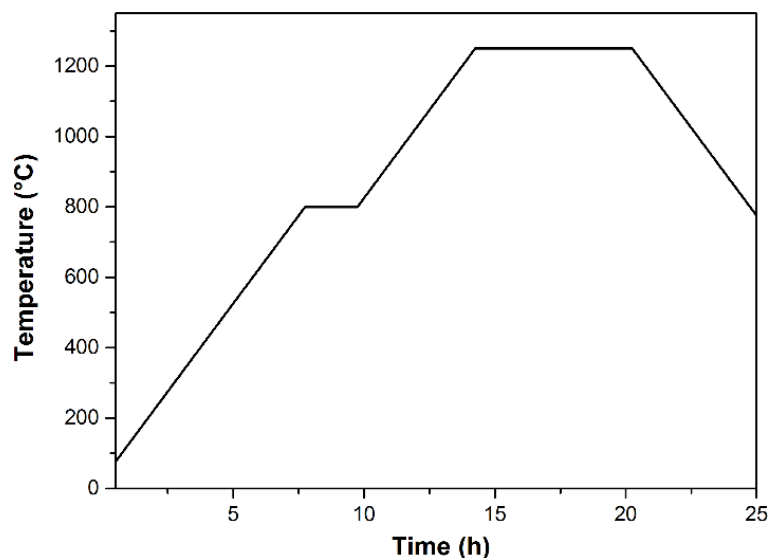


Figure S3. The programmed temperature profile of the conventional sintering of core-shell particles

3. Rietveld refinement

The refinement was conducted by using the FullProf Suite. The structure of the $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.99}\text{CoO}_3$ in the commercial powder as well as in the LSC-CGO core-shell powder was refined in the R-3c space group. The structure of the $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ in the LSC-CGO core-shell powder was refined in the Fm-3m space group. The peak shape of $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.99}\text{CoO}_3$ in both powder diffraction patterns was described by the Cauchy's integral formulation of the Lorentzian function, while the peak shape of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ was described by the Thompson-Cox-Hasting formulation of the pseudo-Voigt function. The scale factor, the zero point, and the unit cell parameters were refined. Considering the small size of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ particles (ca. 6 nm), the peak broadening was assumed to arise purely from the particle size, whereas the strain contribution as well as the instrumental contribution were neglected. The Rietveld refinement residuals are shown in tables below.

Table S1. Rietveld refinement residuals of the diffraction pattern of the raw commercial $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.99}\text{CoO}_3$ powder

Number of Bragg peaks	32
Number of data points	11432
Background points	6
Total number of parameters	13
R_{Bragg}	1.862%
R_{F}	1.889%
Unit cell	$a=b=0.5435\text{nm}$, $c=1.3226\text{nm}$
χ^2	1.10

Table S2. Rietveld refinement residuals of the diffraction pattern of the $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.99}\text{CoO}_3\text{-Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ core-shell powder

Phase	$(\text{La}_{0.6}\text{Sr}_{0.4})_{0.99}\text{CoO}_3$	$\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$
Number of Bragg peaks	32	9
Number of data points	7266	
Background points	6	
Total number of parameters	15	
R_{Bragg}	4.153%	8.731%
R_{F}	4.716%	4.908%
Unit cell	$a=b=0.5434\text{nm}$, $c=1.3226\text{nm}$	$a=b=c=0.5447\text{nm}$
χ^2	1.51	

4. More bright-field TEM images of the $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.99}\text{CoO}_3\text{-Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ core-shell particle

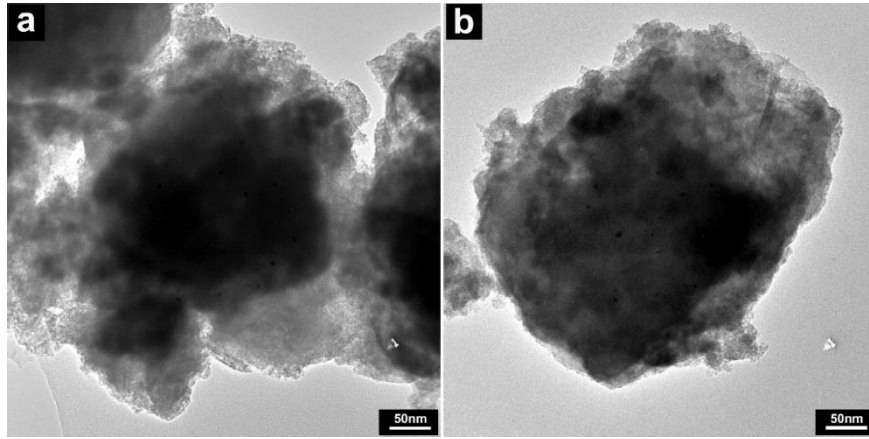


Figure S4. Two additional BF-TEM images of two other core-shell particles

5. An example on the fast Fourier transform (FFT) of a high-resolution image of the $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ shell

The fast Fourier transform (FFT) of a high-resolution image of the $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ shell was processed by the Digital Micrograph, shown in **Figure S5**. Then radiuses of three concentric rings were measured separately. By the reciprocal conversion, measured spacings of the corresponding crystal planes were $1/3.17$ ($= 0.31$ nm), $1/3.69$ ($= 0.27$ nm) and $1/5.28$ ($= 0.19$ nm) separately, which can be assigned to (111), (200) and (220) planes of a $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ crystal.

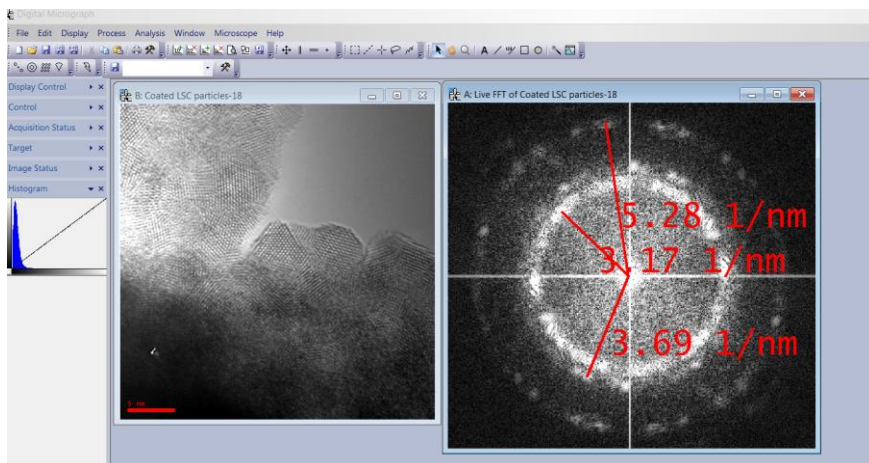


Figure S5. A screenshot presenting the FFT of a high-resolution image of the $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2$ shell and measurements of distances from rings to the concentric center under the reciprocal space; the FFT was done by the Digital Micrograph; the scale bar in the high-resolution TEM image is 5 nm

6. Peak fittings of the XRD pattern of the SPS-densified composite

Figure S6 provides screenshots of the peak fittings of the XRD pattern (using divergent slit size, background subtracted) of the SPS-densified composite to standard patterns in the ICSD database. As observed, all peaks were well fitted to peaks in the stated standard pattern of a certain phase. The two layered double perovskite $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ phases (tetragonal and orthorhombic) have similar reflections especially in the low Bragg angle range, and standard patterns of both phases fit well to the experimental pattern, making it is very difficult to separate the two phases barely by XRD. Nevertheless, the decomposition of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ to the $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ during the SPS process was a certain, whereas the exact composition of the $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ needed to be analyzed by other methods, for example, EDS.

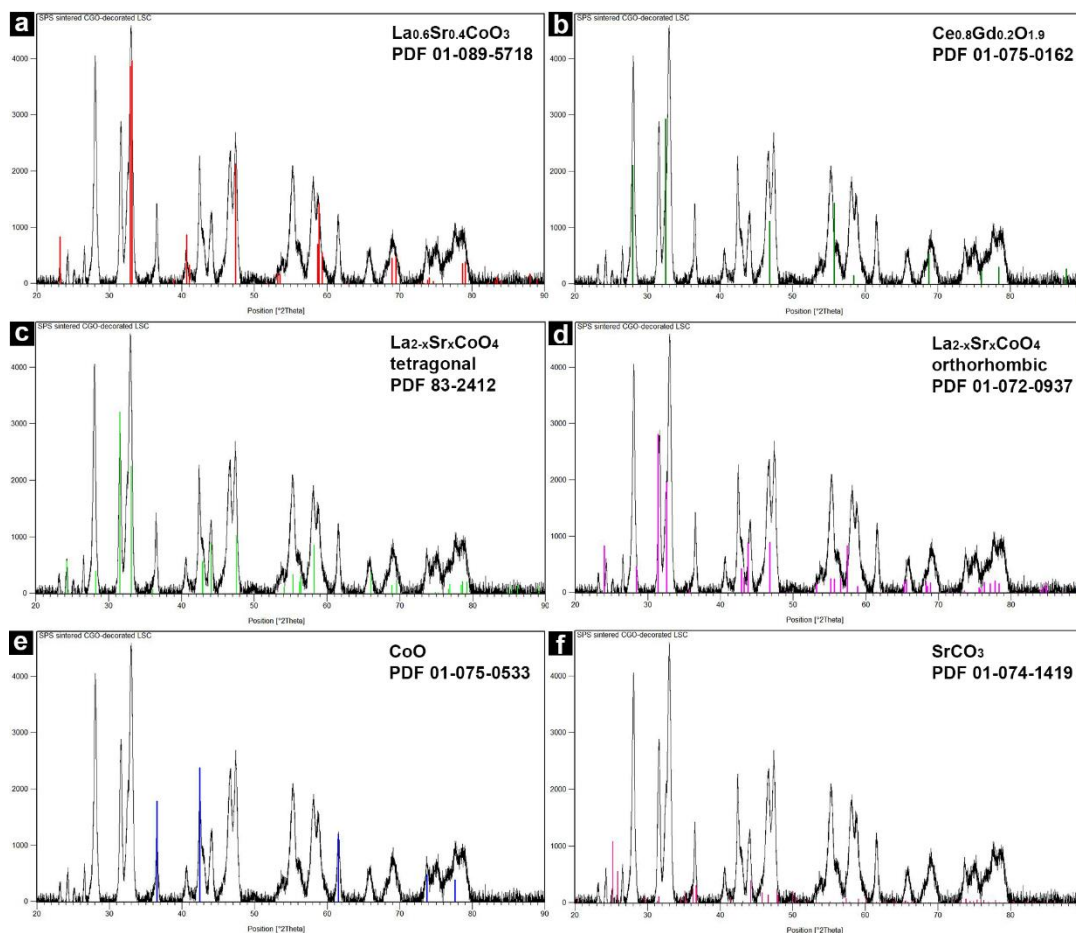


Figure S6. Screenshots of the XRD peak fittings in the software, $2\theta = 20-90^\circ$; (a) $(La_{0.6}Sr_{0.4})CoO_3$ (*space group* R-3c, PDF 01-089-5718); (b) $Ce_{0.8}Gd_{0.2}O_{1.9}$ (*space group* Fm-3m, PDF 01-075-0162); (c) and (d) correspond to the tetragonal ($x=1$, *space group* 14/mmm, PDF 83-2412) and the orthorhombic ($x=0$, *space group* Abma, PDF 01-072-0937) $La_{2-x}Sr_xCoO_4$; (e) CoO (*space group* Fm-3m, PDF 01-075-0533) and (f) $SrCO_3$ (*space group* Pnma, PDF 01-074-1419)

7. Details on analysis of SEM images by the software ThreshAlyzer

ThreshAlyzer is a software based on MATLAB that is designed to analyze the phase distribution in SEM images of polished cross sections. **Figure S7** presents a screenshot of the window of the software. The input of a SEM image gave a histogram of the intensity. By setting a threshold, the phases displaying a contrast/greyscale higher and lower than the threshold were separated in the final segmentation image (used in the main text). The threshold was adjusted until the final segmentation of phases matched what was seen in images by eyes. The output was the final segmentation image, the phase fractions, the equivalent grain diameter/size and the covered volume ratio of grains with the corresponding size.

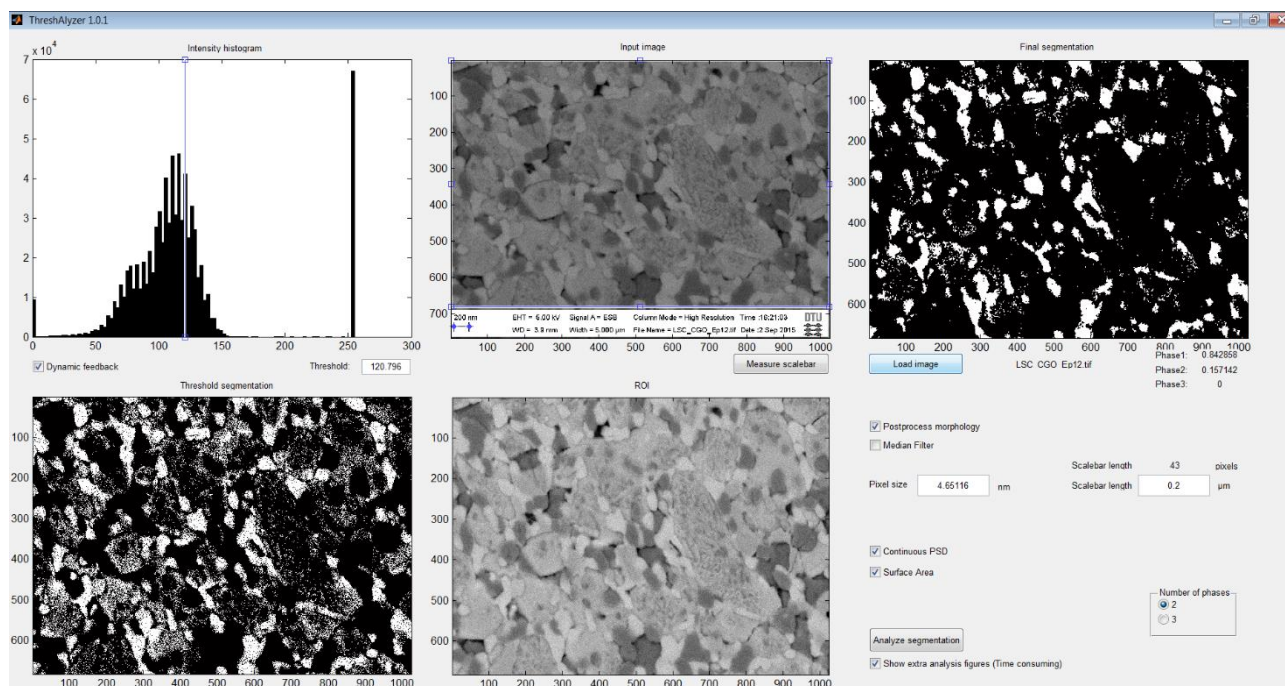


Figure S7. A screenshot of the window of the ThreshAlyzer with an example; from left to right, top: intensity histogram, input image and measure scale bar, and final segmentation; bottom: threshold segmentation, ROI (region of interest) for smaller area analysis, and toggles

An example on output from analyzing a SEM-BSE image of the SPS-densified LSC-CGO sample by the ThreshAlyzer is presented in **Figure S8**. By setting a reasonable threshold value, the white CGO phases were isolated from the others (LSC and its decomposition products that displayed in the darker). The borders were outlined in **Figure S8b**. The final segmentation highlighting the distribution of CGO grains (in the white) and grains of LSC and its decomposition products (as a whole in the black) is presented in **Figure S8c**. The grain size and the covered volume ratio of grains at the size were also given in the output, as presented in **Figure S8d** (CGO grains) and **Figure S8e** (grains of LSC and its decomposition products).

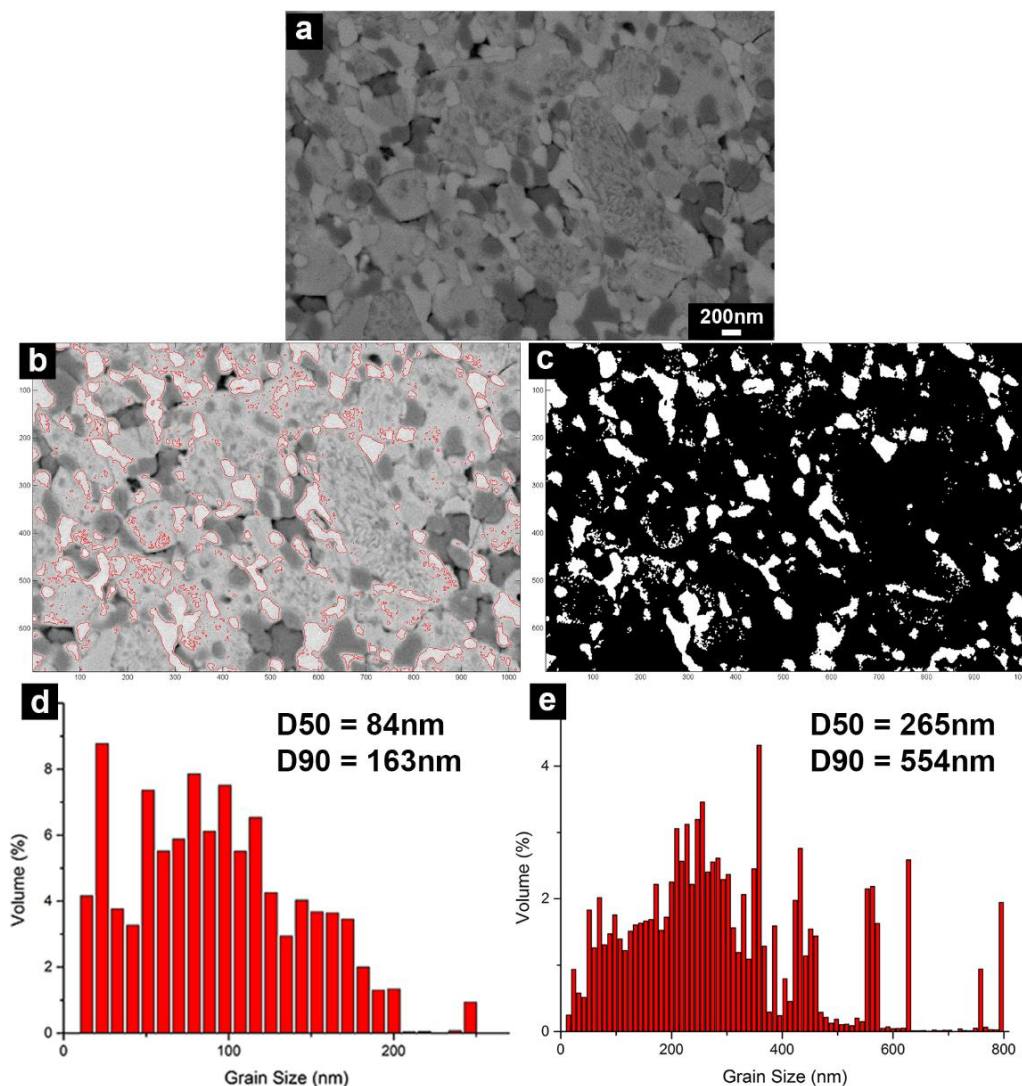


Figure S8. (a) a SEM-BSE image of the polished cross section of the sample of spark plasma sintered LSC-CGO core-shell particles; (b) the border of the white CGO grains is outlined after setting a threshold in the intensity histogram, which can be used as a guide to evaluate the reasonability of the threshold setting values; (c) the final segmentation of the SEM-BSE image, where the CGO grains are highlighted among the others; (d) and (e) present the histograms of ‘grain size *vs* covered volume ratio’ for CGO grains and grains of LSC and decomposition products; D50 and D90 mean a cumulative 50vol% and 90vol% point of diameter respectively

10 SEM-BSE images from different places of the polished cross section of the SPS-densified sample were analyzed. Results of D50 and D90 for all grains are presented in **Table S3**. A statistical quantification shows that 50vol% of CGO grains were below $87(\pm 7)$ nm, while 50vol% of grains of LSC and its decomposition products were below $274(\pm 31)$ nm. It needs to be mentioned that the boundary of grains of LSC and decompositions was not clear in the segmentation, which results in a slightly higher uncertainty in the size quantification of grains. Nevertheless,

the D50 (274 nm) of grains of LSC and decompositions in the SPS-densified sample was close to the D50 (388 nm) of the commercial LSC particle measured by the laser diffraction, which supports the argument that the spark plasma sintering is advantageous in maintaining the original metrics of starting powders.

The output also gave an area ratio of the white phase (CGO) and the black phase (LSC and decomposition products), which was used to estimate the volume ratio of the phases in the SPS-densified sample. On average, the quantification gave a volume ratio of two phases at V[CGO]/V[LSC and decompositions] at 17.2/82.8. In comparison, the molar ratio of CGO to LSC in core-shell particles before sintering was 1:4. The density of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ and $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2$ is 6.274 g cm^{-3} (N. Orlovskaya, et al., *J. Eur. Ceram. Soc.*, vol20, 2000, p51) and 7.2 g cm^{-3} ([https://en.wikipedia.org/wiki/Cerium\(IV\)_oxide](https://en.wikipedia.org/wiki/Cerium(IV)_oxide)) respectively. Assuming that the sample was fully dense, the theoretical calculation gave a volume ratio of V[CGO]/V[LSC and decompositions] at 14.5/85.5. The measured and the theoretical values match each other well.

Table S3. A summary of the D50 and D90 for all grains by analyzing 10 SEM-BSE images of the polished cross section of the SPS-densified LSC-CGO sample

	grains of CGO		grains of LSC and decompositions	
	D50/nm	D90/nm	D50/nm	D90/nm
	103	196	353	547
	93	181	274	554
	84	163	265	554
	88	158	247	470
	81	175	241	414
	88	163	256	479
	82	142	294	482
	88	144	284	442
	84	135	253	428
	79	135	274	526
Average	87	160	274	489
SD	7	18	31	50

The same analysis was also conducted for the SEM-BSE images of the polished cross section of the sample densified by conventional sintering of LSC-CGO core-shell particles. In total, 8 SEM-BSE images were analyzed. The results of D50 and D90 of CGO grains are summarized in **Table S4**. The quantification of the size of grains of LSC is not reported here, as the boundary of the grains could not be determined in the image segmentations. 50vol% of the CGO grains were less than 384($\pm$ 78) nm, showing a remarkable coarsening of grains during the conventional sintering. The measured volume ratio of V[CGO]/V[LSC and Co-rich phases] was 11.7/88.3.

Table S4. A summary of the D50 and D90 for CGO grains by analyzing 8 SEM-BSE images of the polished cross section of the LSC-CGO sample densified by conventional sintering

	D50/nm	D90/nm
	400	758
	217	449
	424	758
	320	680
	403	672
	500	833
	405	730
	404	673
Average	384	694
SD	78	106

Table S5 presents the grain sizes of CGO and LSC (and its decomposition products) of the SPS-densified LSC-CGO composite after thermal treatment. In total, 9 SEM-BSE micrographs were analyzed. After a heat treatment at 700 °C, the mean grain size of CGO increased to 109($\pm$ 16) nm while that of LSC grains increased to 201($\pm$ 23) nm.

Table S5. A summary of the D50 and D90 for all grains by analyzing 9 SEM-BSE images of the polished cross section of the SPS-densified LSC-CGO sample after thermal treatment

	grains of CGO		grains of LSC and decompositions	
	D50/nm	D90/nm	D50/nm	D90/nm
	90	176	490	927
	103	185	481	896
	81	170	555	867
	118	215	393	778
	118	200	407	628
	104	191	433	888
	110	194	448	786
	125	230	336	651
	135	245	305	525
Average	109	201	428	772
SD	16	23	73	133

8. Point EDS analysis on the polished cross section of the sample densified by spark plasma sintering

At an accelerating voltage of 10 kV, EDS analysis was conducted on several selected points (**Figure S9**) on the polished cross section of the SPS-densified sample. It should be noted that the quantification was processed by the embedded ESPRIT Quant Tools for standardless quantitative spectra evaluation and was solely based on data derived from spectra themselves. Nevertheless, the difference of compositions (shown in **Table S6**) at selected points of each greyscale provided a fingerprint to cross check results obtained from the element mapping. The black phase showed a relatively high concentration of La, Co and especially Sr, whereas the white was highly concentrated in Ce and Gd. The ratio of La, Sr and Co determined in the grey phase was more or less close to the stoichiometric value in the raw LSC powder.

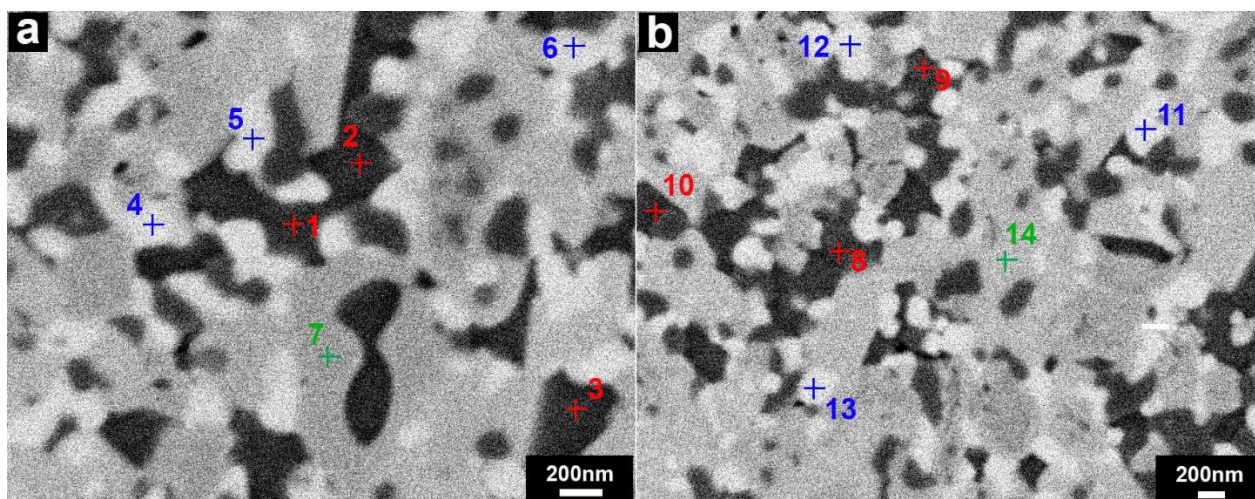


Figure S9. SEM-BSE images of two areas on the polished cross section of the SPS-densified sample; all selected points for EDS analysis are labeled by cross lines

Table S6. Atomic compositions determined by the point EDS analysis (unit: atomic percent)

	Point	La	Sr	Co	Ce	Gd
Black	#1	20.01	49.36	14.41	16.22	0
	#2	27.99	47.29	14.84	9.57	0.30
	#3	9.40	54.82	17.80	16.85	1.13
	#8	9.44	67.06	11.46	12.04	0
	#9	16.35	40.39	17.78	25.48	0
	#10	11.75	27.62	27.11	14.99	3.42
White	#4	23.61	11.17	7.54	46.82	10.86
	#5	18.50	12.36	11.33	46.38	11.43
	#6	25.12	16.55	10.14	41.67	6.52
	#11	18.53	8.60	8.64	54.50	9.74
	#12	16.07	17.03	11.44	46.21	9.25
	#13	14.80	3.77	28.00	44.10	9.33
Grey	#7	34.67	20.42	25.12	18.11	1.68
	#14	44.33	20.18	19.73	11.85	3.92

9. Element mapping by EDS on the polished cross section of the LSC-CGO sample densified by the conventional sintering

Figure S10 presents a mapping of La L (b), Co K (c) and Ce L (d) on the polished cross section (a) of the sample densified by conventional sintering of LSC-CGO core-shell particles. As observed, the black phase was enriched in Co, while the white phase had a high concentration of Ce. Dopants including Sr and Gd are not presented here, as they were not depleted from the doped phases, as demonstrated by the element line scan analysis shown in the main text.

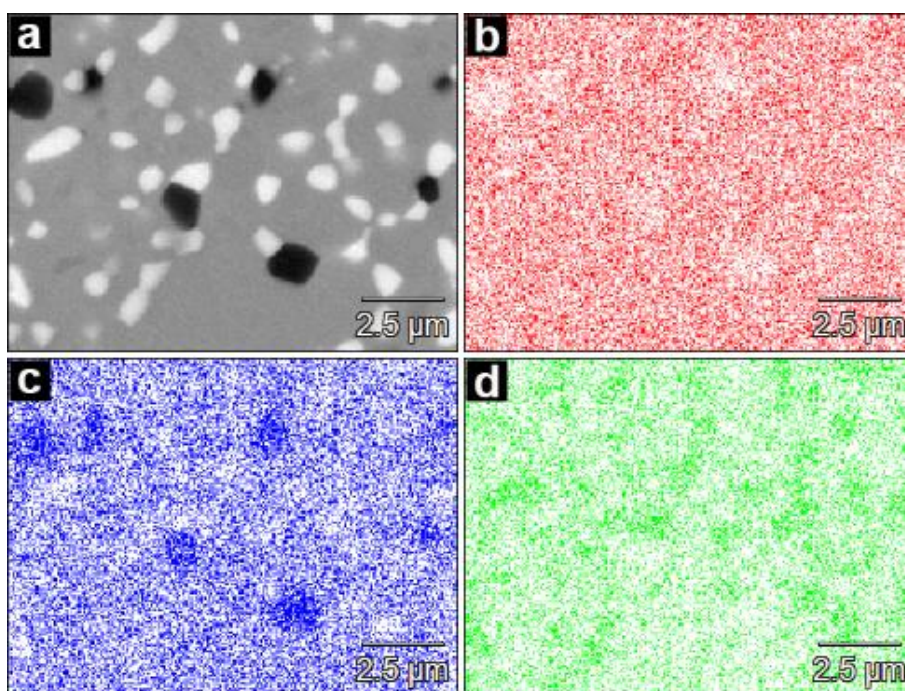


Figure S10. (a) a SEM-BSE image of the polished cross section of the LSC-CGO sample densified by conventional sintering; (b), (c) and (d) are element maps of La L α , Co K α and Ce L α , respectively

9. Additional microscopy images of the samples densified by SPS and conventional sintering

Figure S11 presents SEM-BSE microscopy images of three additional areas for each sample, **a-c** are from the SPS-densified sample and **d-e** are from the conventionally sintered sample. A finer structure can be observed in the SPS-densified sample.

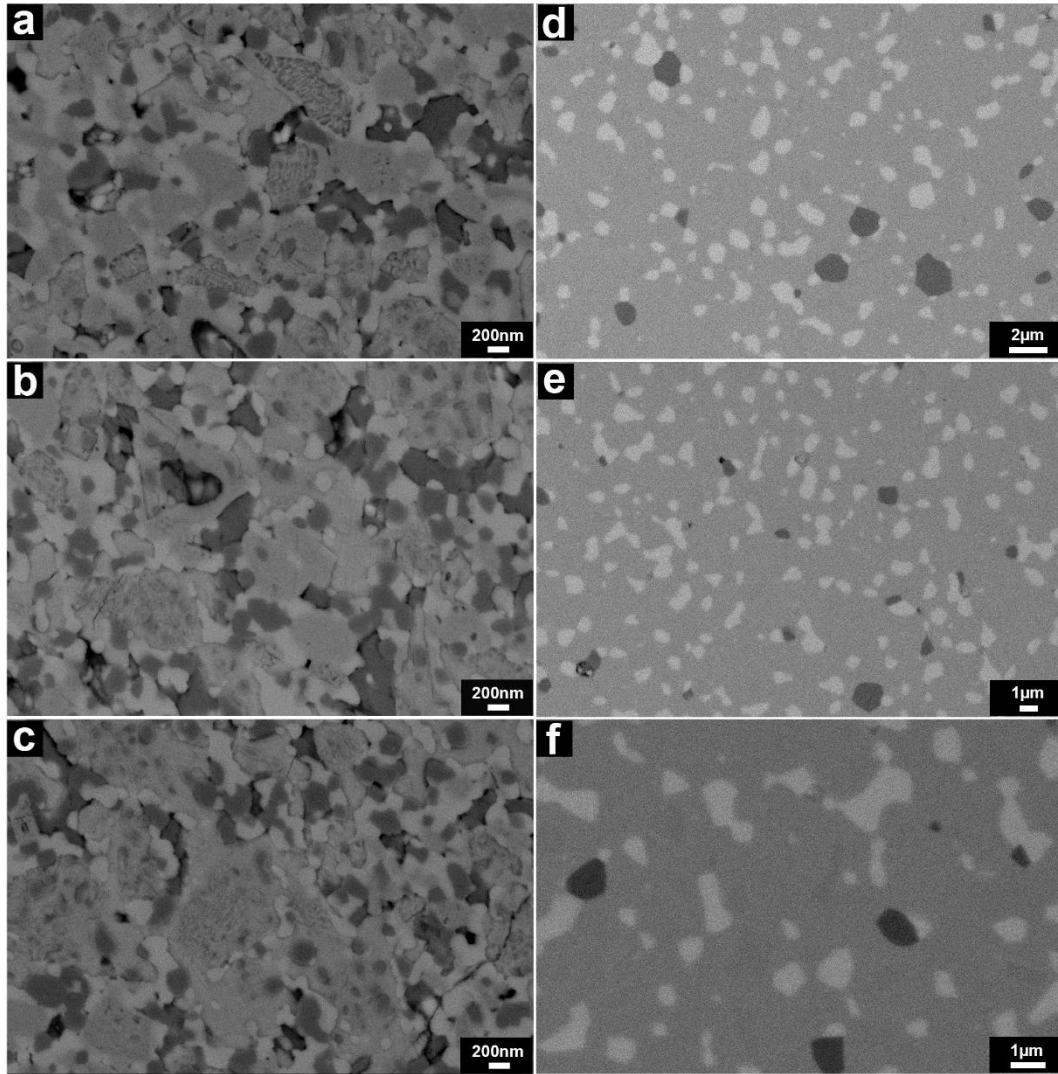


Figure S11. a-c (scale bar 200 nm) are three independent areas of the SPS-densified sample, and d-e (scale bar 1 μm , 1 μm and 2 μm separately) are three independent areas of the sample densified by the conventional sintering. All images were recorded by processing BSEs

Figure S12 presents microscopy images of the fracture surface of the samples densified by SPS (**a** and **b**) and the conventional sintering (**c** and **d**).

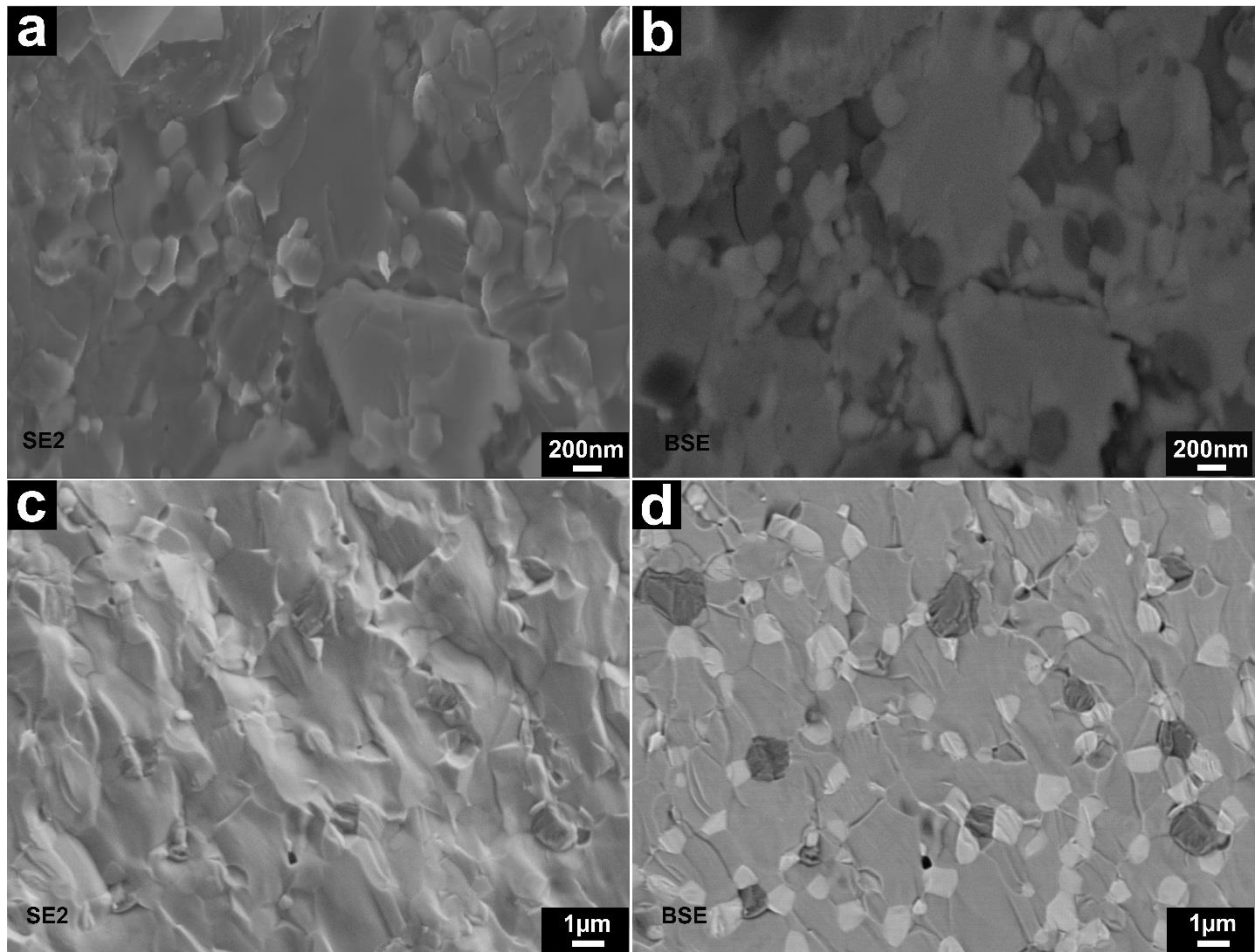


Figure S12. Fracture surface of the samples densified by SPS (a and b) and by conventional sintering (c and d). For each selected area, SE2 and BSE images were recorded simultaneously