

Electronic Supporting Information

Accurate Control of Stoichiometry and Doping in Barium Stannate Perovskite Oxide Nanoparticles

William Shepherd^a, Michael Wilms^a, Joel van Embden^a, Enrico Della Gaspera^{a,}*

^a School of Science, RMIT University, Melbourne VIC 3000, Australia

Corresponding author: *enrico.dellagaspera@rmit.edu.au

Experimental details

Materials

Barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, 99%, Sigma Aldrich), tin chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, 98%, Sigma Aldrich), citric acid ($\text{C}_6\text{H}_8\text{O}_7$, 99.5%, Sigma Aldrich), lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.99%, Sigma Aldrich), hydrogen peroxide solution (H_2O_2 , 30% w/v, ROWE Scientific), ammonium hydroxide solution (NH_4OH , 25% v/v, Chem-Supply). All chemicals were used without further purification and all syntheses were conducted under ambient laboratory conditions.

Synthesis of BaSnO_3 and La-doped BaSnO_3 nanoparticles

In a typical synthesis, 0.5 mmol of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.5 mmol $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ were dissolved in 8.5 ml of 30% H_2O_2 solution in the presence of citric acid (0.25 mmol) in a glass scintillation vial. The pH of this solution was measured as ~ 0.2 . The vial was then placed in a preheated water bath at 60 °C and left for 15 minutes to reach the set temperature. Then 3 mL of 25% ammonia solution was added quickly under strong stirring, and a white precipitate appeared instantly. The pH of the suspension after the addition of ammonia was ~ 9.2 . After 1 hour of stirring the resulting white suspension was placed in a 50 mL centrifuge tube and deionised (DI) water was added to fill the tube. The sample was ultrasonicated for 5 minutes and centrifuged at 4400 rpm for 5 minutes. The supernatant was discarded and the precipitate was re-dispersed in DI water through sonication, and centrifuged again. This process was repeated 3-5 times, until the pH of the supernatant was ~ 7 . At this point, the final wash was done using ethanol, and after discarding the supernatant, the CSMC precursor was dried in an oven at 70 °C overnight. The precursor was then annealed at the desired temperature (from 300 °C to 900 °C) for 2 hours in a muffle furnace. Variation from these typical reaction conditions include: (i) adding ammonia slowly (dropwise); (ii) varying the amount of ammonia, using either 1, 2.3, 3, 4 or 6 mL ammonium hydroxide solution, corresponding to ammonia/metal molar ratios of 13, 30, 40, 53, 80; (iii) varying the amount of citric acid, using either 0, 0.25, 0.5, 2 or 5 mmol; (iv) using different “standing times” at 60 °C (5, 15, 45, 120 min) before precipitating the CSMC with ammonia; (v) changing the pH of the precursor solution before the addition of ammonia using 2M HCl, with the following $\text{HCl}/(\text{Ba}+\text{Sn})$ molar

ratios: 0, 2, 4, 8. The lowest pH achieved was ~ 0.1 , and the amount of ammonia added was adjusted so that the final pH was always ~ 9.2 .

The synthesis of doped nanoparticles was conducted using the same protocol described above, and replacing a certain amount of barium with lanthanum, keeping the total amount of moles of metal constant. The lanthanum doping level (D) is then defined as

$$D(\%) = \frac{n_{La}}{(n_{Sn} + n_{Ba} + n_{La})} \times 100$$

where n is the number of moles.

Characterization techniques

X-ray diffraction (XRD) patterns of powder samples were collected using a Bruker D4 Endeavor diffractometer equipped with a Cu-K α radiation source and operated at 40 kV and 35 mA. The crystallite size was evaluated with the Scherrer relationship using the full width at half-maximum of the diffraction peaks fitted using Lorentzian functions. For each sample the extracted size values from each of the diffraction peaks were averaged and the error was calculated as one standard deviation. Fourier transform infrared (FTIR) spectroscopy was carried out using a Perkin-Elmer Frontier spectrometer equipped with a Pike GladiATR attenuated total reflectance (ATR) stage. For La-doped BSO samples, a gradient analysis was performed to evaluate the extent of the free carrier absorption in the infrared region. The FTIR spectra were analyzed in the range 1700-2700 cm $^{-1}$ due to the absence of absorption peaks, and approximated to linear functions. Then the derivative of the spectra was calculated and the values were compared as a function of doping level and annealing temperature. The final data are presented in Figure 4 as the average of at least 3 independent measurements. Scanning electron microscopy (SEM) images were acquired on a FEI Verios 460L SEM operated at 2 kV and 13 pA. Energy dispersive X-ray (EDX) spectra were acquired on a Nova 200 NanoSEM with a voltage of 18 kV. The relative Sn, Ba and La composition for each sample was averaged on at least 6 independent measurements. Thermogravimetric analysis (TGA) was conducted on a Perkin Elmer Pyris 1 instrument at a heating rate of 5 $^{\circ}$ C/min in air. Optical absorption spectra of BSO powders were acquired with a Cary 7000 UV-Vis-NIR spectrometer equipped with an integrating sphere and a centermount sample holder.

Figure S1

Thermogravimetric analysis (TGA) curves for BSO CSMC precursor. A total weight loss of ~15% is observed, consistent with the removal of organic ligands and of peroxy groups.

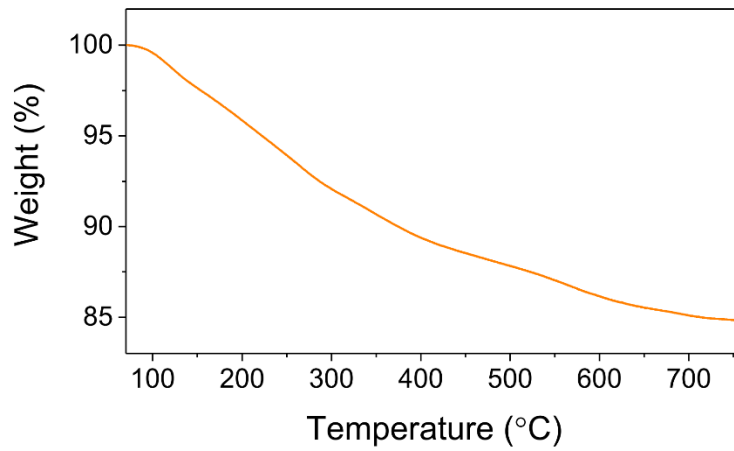


Figure S2

XRD patterns for BSO CSMC precursor synthesized with varying amounts of ammonia. The crystallite size evaluated with the Scherrer relationship is also reported

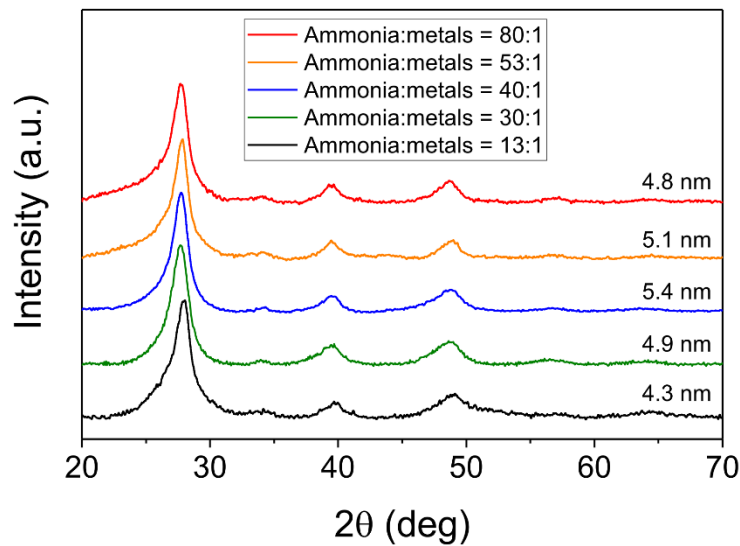


Figure S3

XRD patterns for BSO CSMC precursor synthesized by quickly injecting or slowly dripping the same amount of ammonia solution. The inset shows a zoomed view of the main diffraction peak.

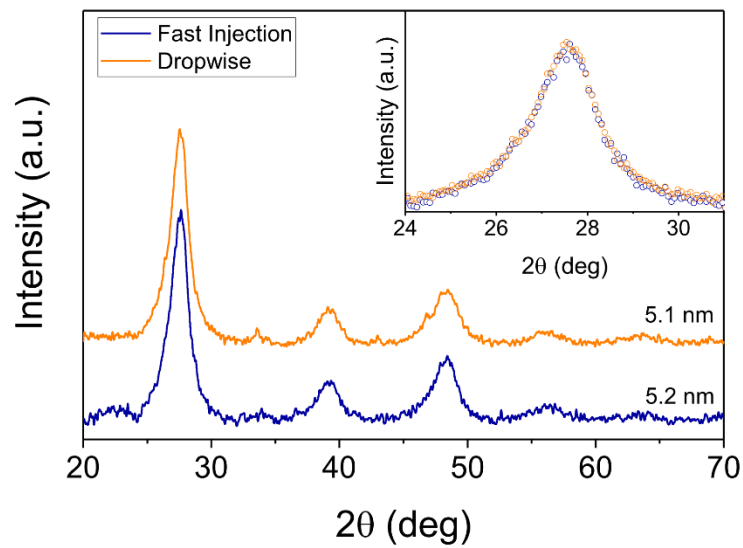


Figure S4

XRD pattern for BSO powders annealed at 300 °C (top panel) and 500 °C (bottom panel) as a function of the amount of citric acid used in the synthesis. The peaks marked with stars are assigned to BaCO₃ impurities. These are formed due to carbonation of BSO in ambient air, a well known effect in Ba-containing oxides including BaSnO₃ and BaTiO₃.

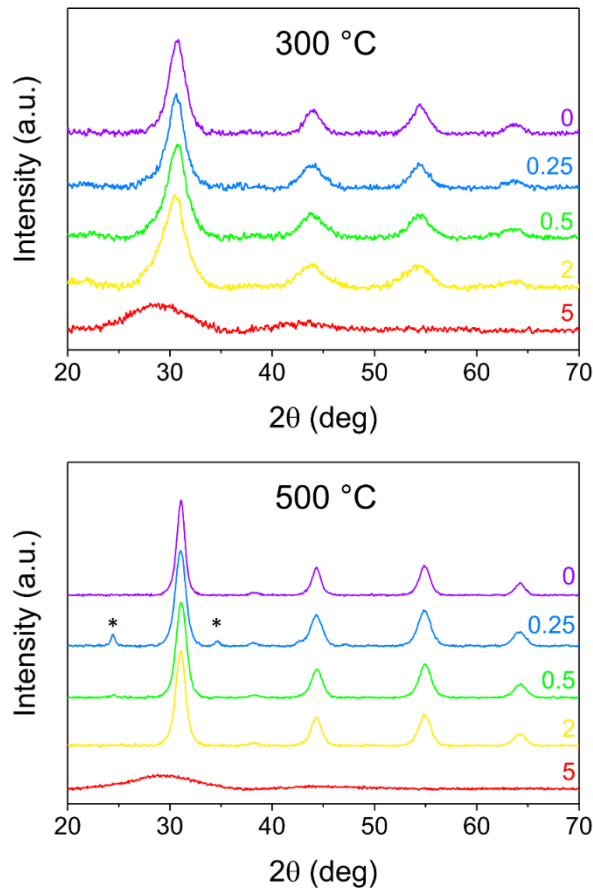


Figure S5

SEM images of BSO CSMC precursor and of BSO powders annealed at 300 °C and 500 °C. The scale bar is 200 nm and is common to all three micrographs.

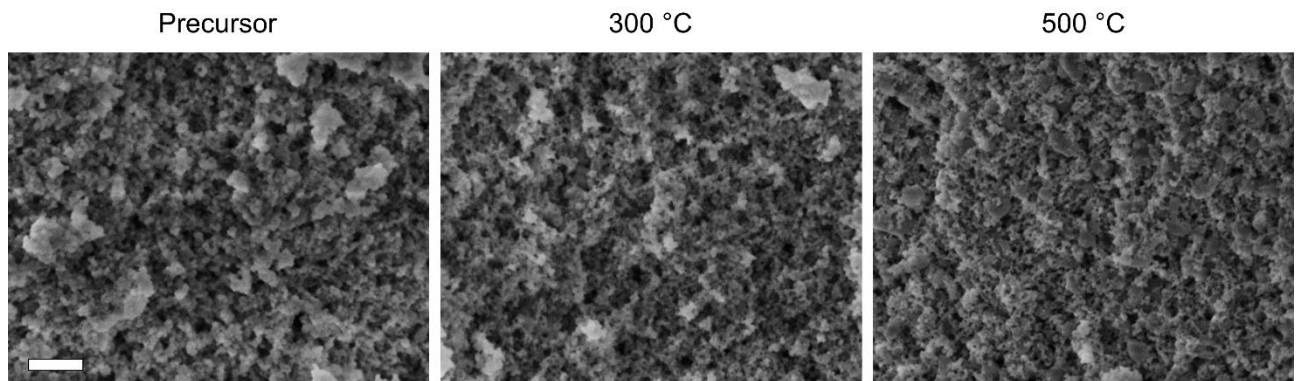


Figure S6

XRD pattern for BSO precursor and annealed BSO powders as a function of the standing time before the addition of ammonia. A clear degradation of crystallinity is observed at longer standing time, consistent with the large off-stoichiometry detected with EDX. Evidence of separate SnO_2 nanocrystals is also observed (peaked marked by stars according to ICDD No. 41-1445). The peak highlighted by a dashed box is due to the sample holder.

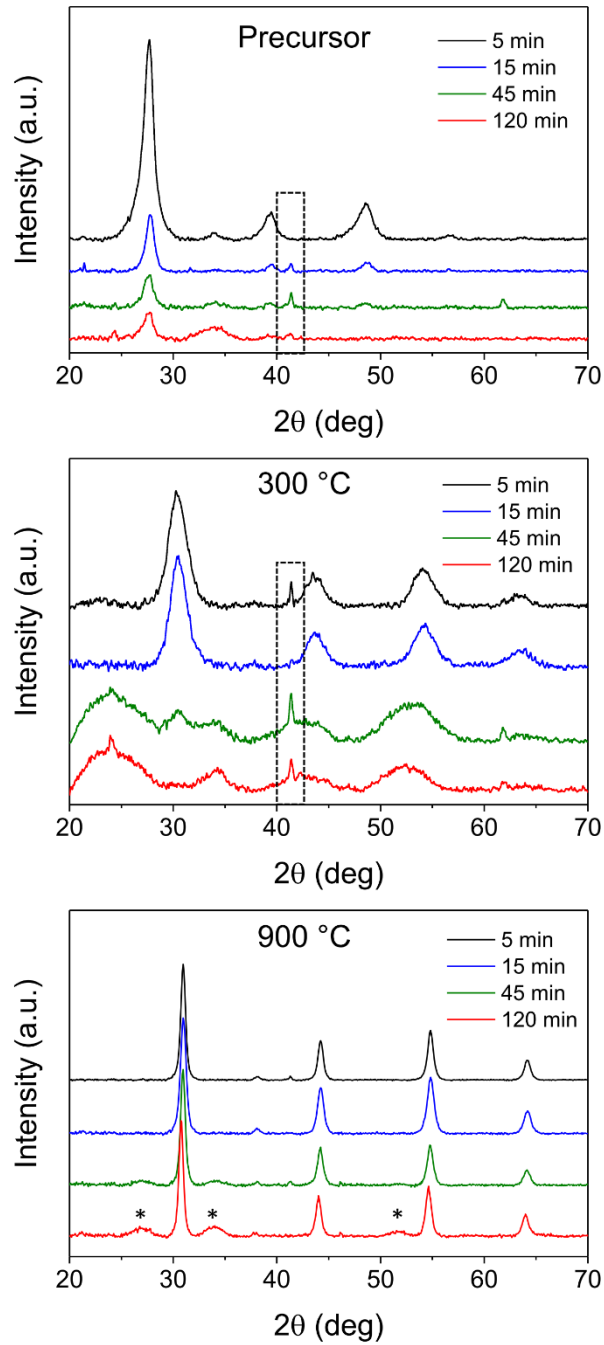


Figure S7

In order to investigate the nature of the precipitates potentially occurring in our reactions, we tested the stability over time at 60°C of the following solutions:

- A) $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in water
- B) $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in 30% H_2O_2
- C) $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in 30% H_2O_2 with 8 equivalent HCl

Solution A became cloudy after ~20 minutes of stirring, with white precipitates clearly visible. Solution B and C (which represent the standard conditions and our acidified conditions) appear fully clear, without any precipitate after 2 hours of stirring (top left panel in the figure). However, we showed the colloidal nature of solution B by shining a red laser beam (bottom left panel). Interestingly, no Tyndall effect is observed from solution C. From XRD analyses of the precipitate collected from solution A, we could identify nano-sized aggregates of tin oxide (right panel). Tin (IV) hydroxides are rather unstable and over time convert to more stable oxides, especially when heated. We also prepared solution A at room temperature: after several hours of stirring, we observed the formation of precipitates, and XRD analyses of these precipitates indicated the formation of even smaller clusters that could be identified as either SnO_2 (red reference pattern), or $\text{Sn}_6\text{O}_4(\text{OH})_4$ (black reference pattern). However, given the very small size of these clusters (<2 nm from Scherrer analysis of diffraction peaks) a definitive identification of the exact phase is not feasible.

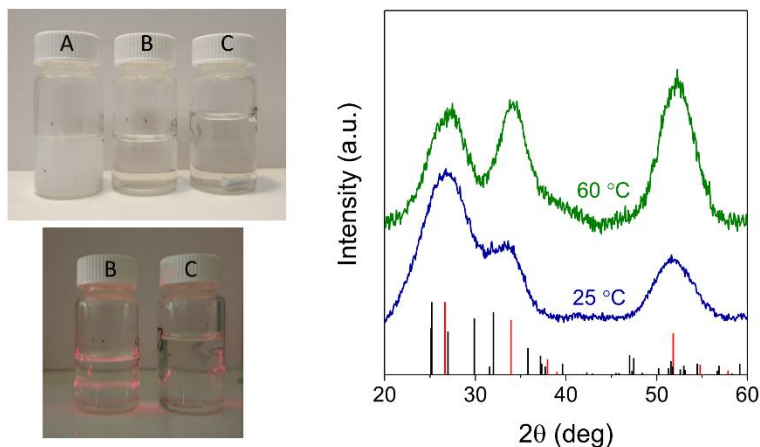


Figure S8

Left: XRD patterns for BSO CSMC prepared from solution at different metal concentrations (keeping Sn:Ba = 1) and 1 hour standing time. The predicted diffraction peak positions for BSO CSMC and SnO₂ are reported at the bottom in black and red, respectively. The orange trace is the precipitate collected from the 0.5 mmol sample prior to the addition of ammonia and shows very broad peaks ascribed to SnO₂. A separate experiment was carried out adding ammonia to the 0.5 mmol sample ignoring the initial precipitation, inducing the formation of BSO CSMC. Such sample shows the XRD signatures of both BSO CSMC and SnO₂ (blue trace). Right: Tin and barium atomic percentages evaluated from EDX on the CSMC precursors, and on the precipitate collected from the 0.5 mmol sample prior to the addition of ammonia.

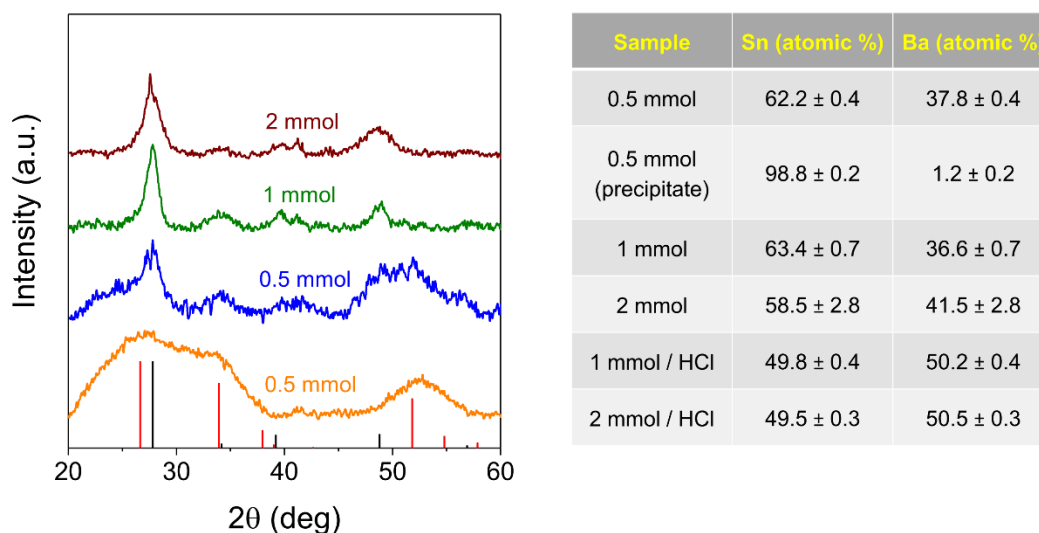


Figure S9

SEM images of BSO nanoparticles both as CSMC and as annealed (300 °C) perovskite nanocrystals as a function of standing time and HCl amount. Scale bars are 200 nm.

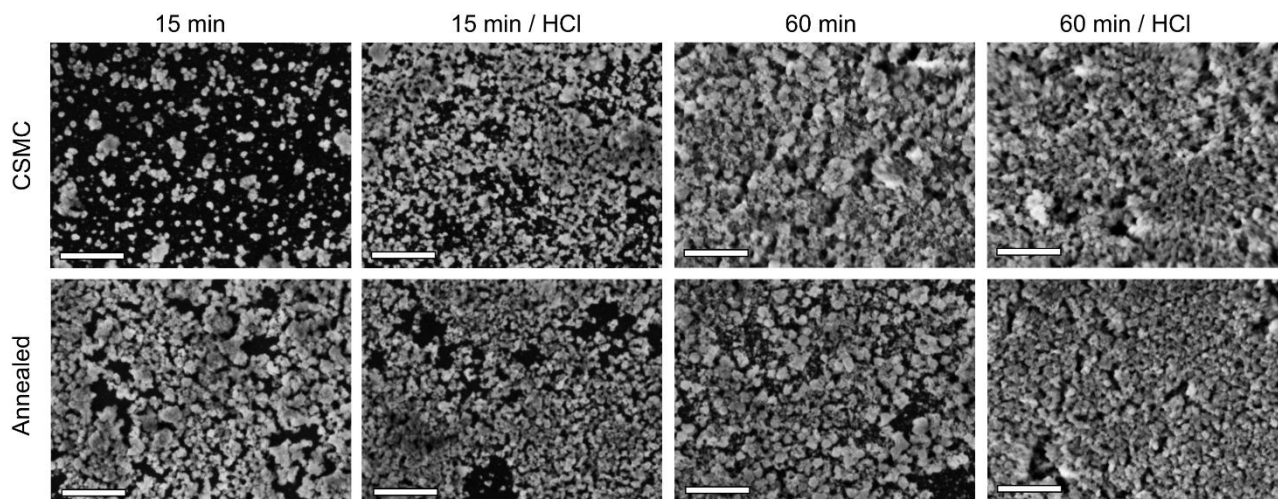


Figure S10

XRD pattern of BSO prepared from purposefully off-stoichiometric CSMC precursor after annealing at 300 °C. The reported values identify the experimental Sn/Ba ratio. The peaks marked by a star are due to the XRD sample holder.

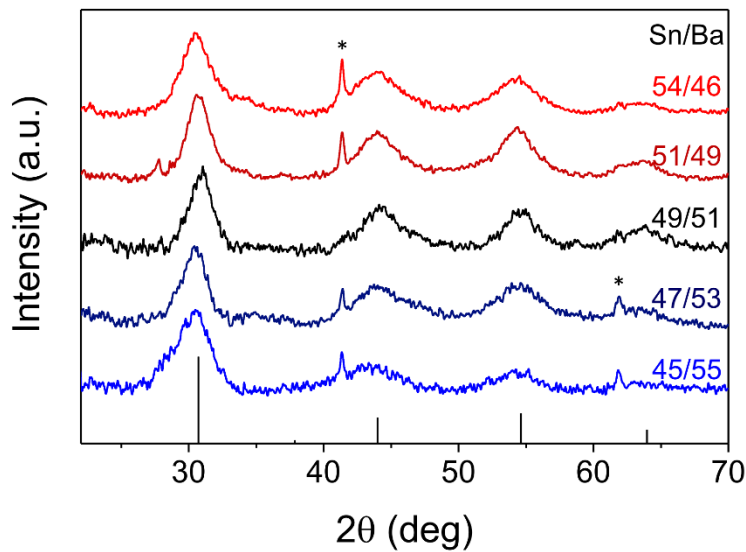


Figure S11

XRD pattern of 5% La-doped BSO both as CSMC precursor and annealed powders.

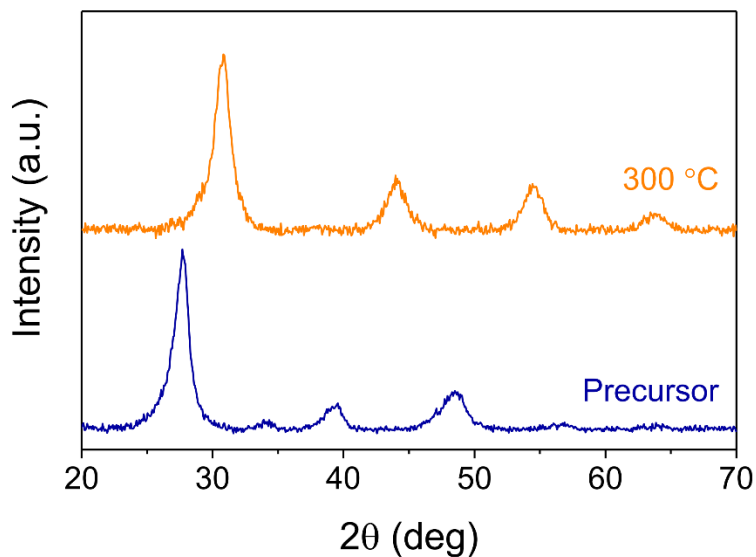


Figure S12

FTIR spectra of LBSO powders after annealing at 900 °C synthesized with different amounts of lanthanum. The digital photograph of the prepared powders is shown at the bottom.

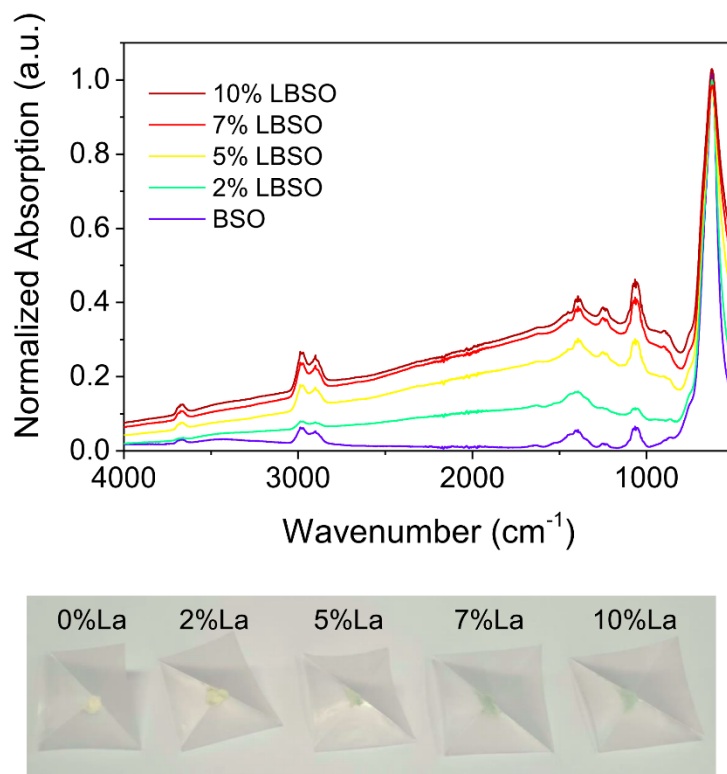


Figure S13

SEM images of BSO and LBSO nanoparticles as a function of La doping both as CSMC precursors and as annealed (900 °C) perovskite nanocrystals. Scale bars are 200.

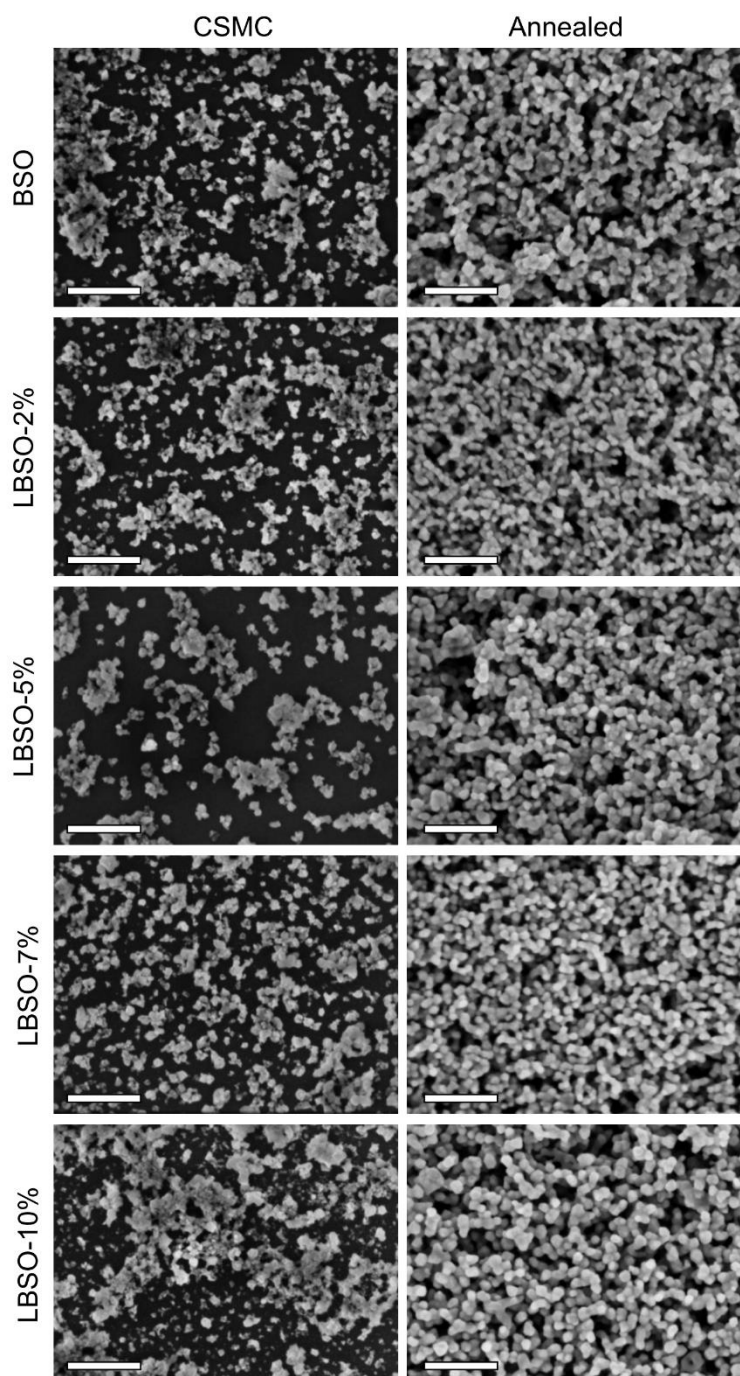


Figure S14

FTIR spectra of LBSO powders doped with 10% La after annealing at different temperatures. The digital photograph of the prepared powders is shown at the bottom.

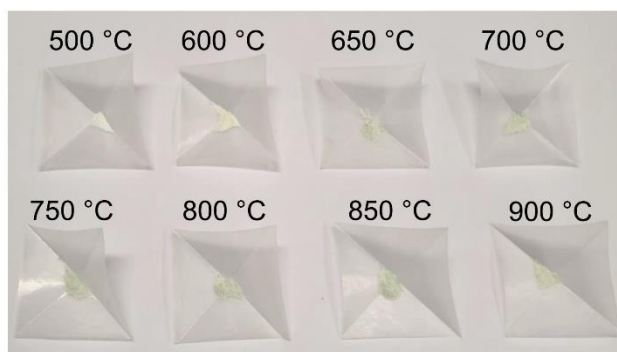
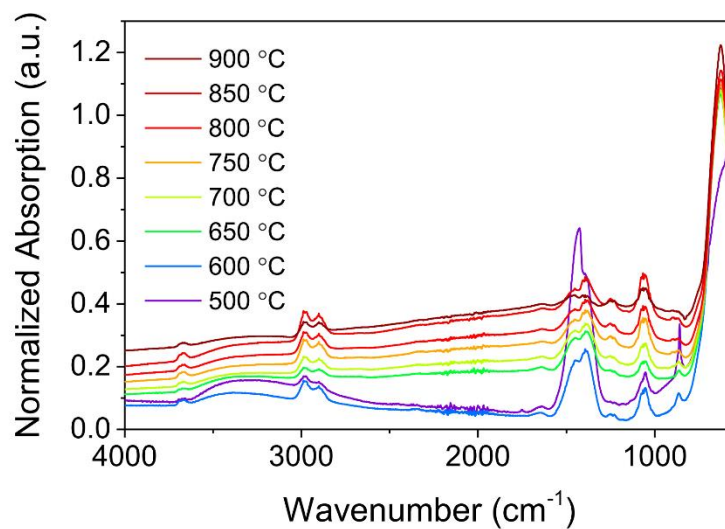


Table S1

Frequency range and respective assignment for the main FTIR peaks detected in CSMC precursor and crystalline BSO. The presence of carbonate anions (CO_3^{2-}) vibrational peaks is due to the tendency of barium to carbonate in air.

Frequency (cm^{-1})	Assignment mode	Reference
3300-3000	$\nu(\text{O-H})$ stretching	[1], [2], [3], [4]
1650-1640	$\delta(\text{H}_2\text{O})$ scissoring	[2], [3], [4]
1560-1540	$\delta(\text{H}_2\text{O})$ scissoring down shifted due to cation interactions	[5]
1380-1430	$\delta(\text{O-O-H})$ scissoring	[1], [2]
1385-1440	$\nu(\text{C-O})$ stretching (in CO_3^{2-})	[2], [4], [6]
~1420	$\nu_s + \nu_{as}$ (Ba-O) symmetric and asymmetric stretching	[6]
1040-1000	$\delta(\text{Sn-OH})$ scissoring	[2]
855-865	$\nu(\text{O-O})$ stretching	[1], [2]
860-870	$\delta \text{C-O}$ (in CO_3^{2-}) out of plane bending	[4], [6]
770-450	$\delta(\text{Sn-O-O})$, $\nu(\text{Sn-O})$ scissoring and stretching	[2], [3]

Table S2

Compositional analysis (from EDX) for BSO samples synthesized with different Sn/Ba ratios using our optimized acid-assisted reaction. The atomic percent of the metals is given assuming Sn + Ba = 100%.

Nominal values		Experimental values from EDX			
Composition	Sn/Ba	Sn (%)	Ba (%)	Sn/Ba	Composition
$\text{Ba}_{1.13}\text{Sn}_{0.87}\text{SnO}_3$	0.77	45.2±0.5	54.8±0.5	0.82±0.2	$\text{Ba}_{1.10}\text{Sn}_{0.90}\text{SnO}_3$
$\text{Ba}_{1.05}\text{Sn}_{0.95}\text{SnO}_3$	0.9	47.1±0.7	52.9±0.7	0.89±0.02	$\text{Ba}_{1.06}\text{Sn}_{0.94}\text{SnO}_3$
BaSnO_3	1	49.2±0.5	50.8±0.5	0.97±0.02	$\text{Ba}_{1.02}\text{Sn}_{0.98}\text{O}_3$
$\text{Ba}_{0.95}\text{Sn}_{1.05}\text{SnO}_3$	1.1	51.1±0.4	48.9±0.4	1.05±0.1	$\text{Ba}_{0.98}\text{Sn}_{1.02}\text{SnO}_3$
$\text{Ba}_{0.87}\text{Sn}_{1.13}\text{SnO}_3$	1.3	53.9±0.4	46.1±0.4	1.17±0.02	$\text{Ba}_{0.92}\text{Sn}_{1.08}\text{SnO}_3$

Table S3

Compositional analysis (from EDX) for LBSO samples synthesized with varying La loadings. The atomic percent of the three metals is given assuming Sn + Ba + La = 100%.

Nominal values		Experimental values from EDX				
Composition	La (%)	Sn (%)	Ba (%)	La (%)	Sn/(Ba+La)	Composition
BaSnO ₃	0	50.4±0.3	49.4±0.2	0.2±0.2 ^a	1.015±0.014	Ba _{0.99} Sn _{1.01} O ₃
Ba _{0.96} La _{0.04} SnO ₃	2	50.6±0.7	47.3±0.4	2.1±0.3	1.025±0.028	Ba _{0.95} La _{0.04} Sn _{1.01} O ₃
Ba _{0.9} La _{0.1} SnO ₃	5	50.4±0.3	44.0±0.3	5.6±0.3	1.017±0.018	Ba _{0.88} La _{0.11} Sn _{1.01} O ₃
Ba _{0.86} La _{0.14} SnO ₃	7	50.7±0.4	42.4±0.5	6.9±0.2	1.027±0.023	Ba _{0.85} La _{0.14} Sn _{1.01} O ₃
Ba _{0.8} La _{0.2} SnO ₃	10	51.0±0.3	38.4±0.3	10.6±0.3	1.042±0.016	Ba _{0.77} La _{0.21} Sn _{1.02} O ₃

^a Value obtained by forcing the EDX software to fit the La peak in an undoped sample. This is indicative of the noise associated with the measurements.

Table S4

Dopant amount (from EDX) for a nominal 10%LBSO as a function of annealing temperature.

Temperature (°C)	Measured La doping (%)
500	10.43 ± 0.29
600	10.49 ± 0.27
650	10.57 ± 0.27
700	10.63 ± 0.28
750	10.26 ± 0.20
800	10.47 ± 0.41
850	10.74 ± 0.32
900	10.47 ± 0.27

References

1. S. S. Shin, E. J. Yeom, W. S. Yang, S. Hur, M. G. Kim, J. Im, J. Seo, J. H. Noh and S. I. Seok, *Science*, 2017, **356**, 167-171.
2. S. Sladkevich, V. Gutkin, O. Lev, E. A. Legurova, D. F. Khabibulin, M. A. Fedotov, V. Uvarov, T. A. Tripol'skaya and P. V. Prikhodchenko, *Journal of Sol-Gel Science and Technology*, 2009, **50**, 229-240.
3. M. Epifani, M. Alvisi, L. Mirengi, G. Leo, P. Siciliano and L. Vasanelli, 2001, **84**, 48-54.
4. W. Lu and H. Schmidt, *Ceramics International*, 2008, **34**, 645-649.
5. R. Kevorkyants, A. V. Rudakova, Y. V. Chizhov and K. M. Bulanin, *Chemical Physics Letters*, 2016, **662**, 97-101.
6. W. Lu and H. Schmidt, *Journal of Sol-Gel Science and Technology*, 2007, **42**, 55-64.