

1. Overall work

The overall process involved in synthesis and characterization of the present work is pictorially represented in fig.s1.

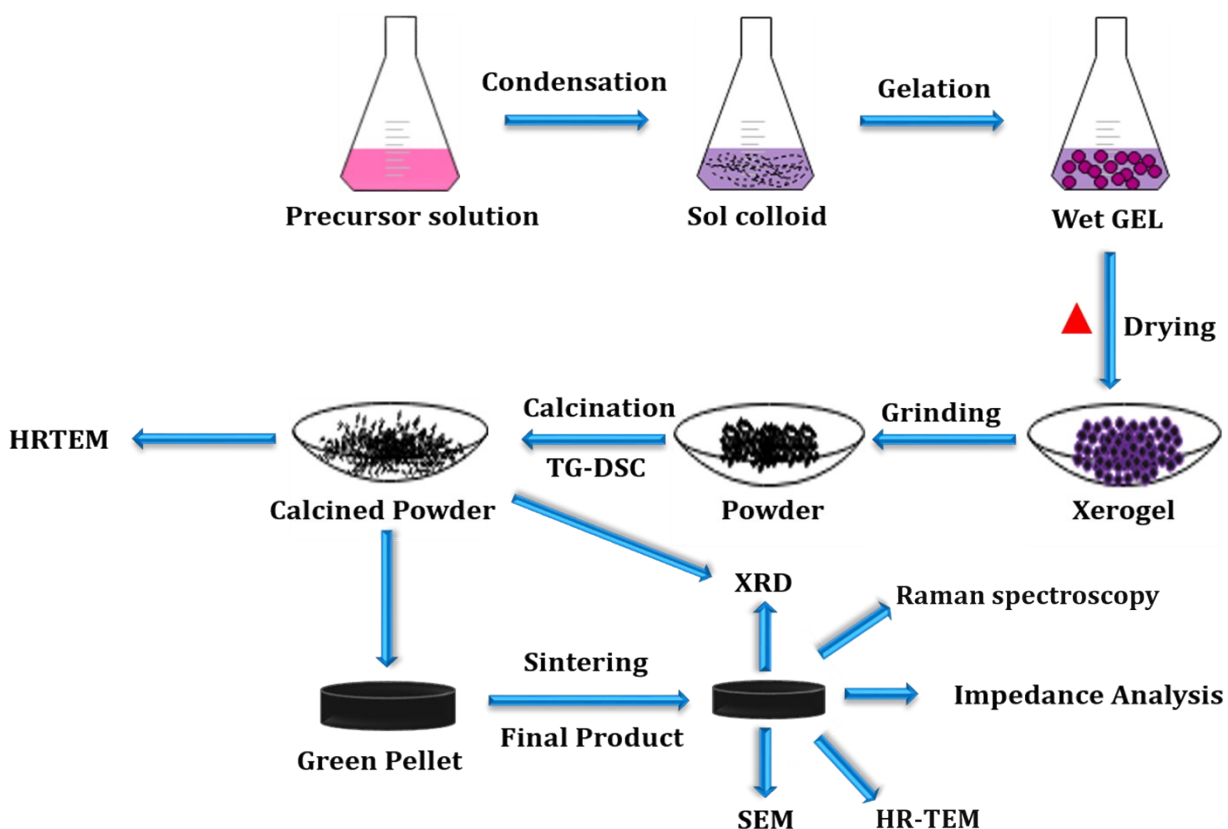


Fig.s1 Pictorial representation of overall synthesis and characterization process

2. Thermal analysis using TG/DSC

Pure and Lithium, Magnesium, Calcium, Strontium and Barium substituted Lanthanum Cobaltites were synthesized using sol-gel method. Thermogravimetry (TG)-differential scanning calorimetry (DSC) data of the xerogel obtained during the synthesis are shown in fig.s2. Several stages of weight loss in TG curve indicate the removal of volatile byproducts on increasing the temperature. Formation of stable phase is apparent after around 790°C. Based on these

observations the xerogel corresponding to various compositions were calcined separately at 800°C for 2 hours to obtain black colored powders of undoped and doped LaCoO_3 .

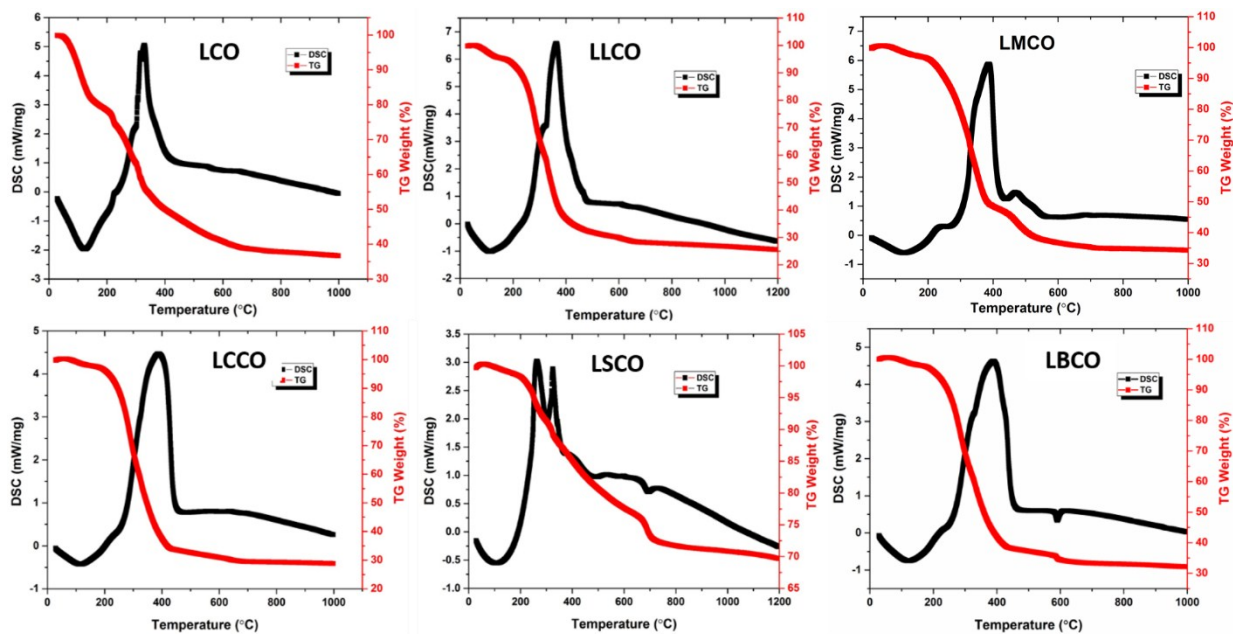


Fig.s2 TG-DSC data of xerogel powders obtained during the sol-gel synthesis method

3. Rietveld analysis of samples

Rietveld analysis of LCO, LLCO, LMCO, LCCO, LSCO and LBCO are shown in fig.s3-fig.s8 respectively.

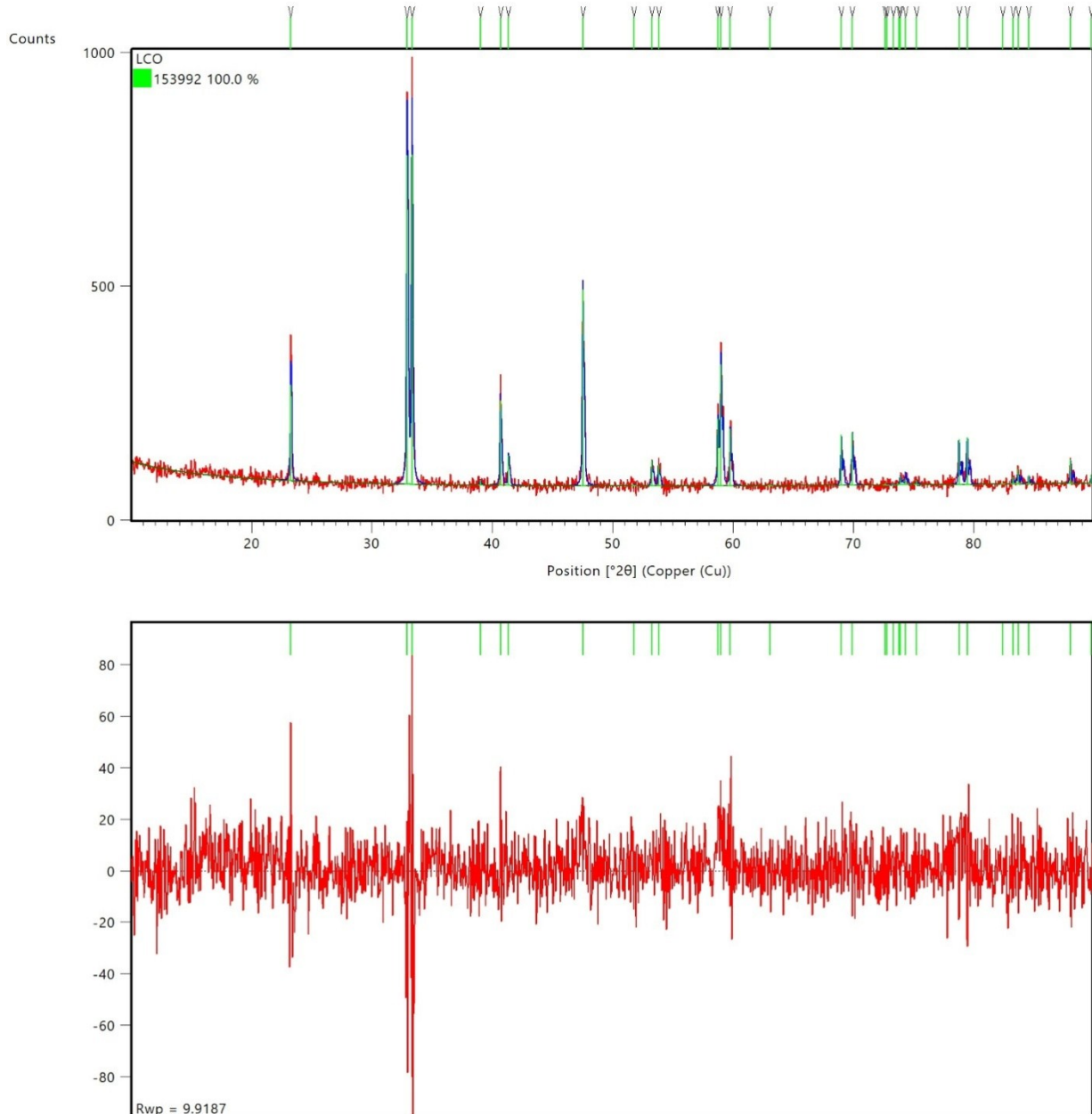


Fig.s3 Rietveld analysis of LCO

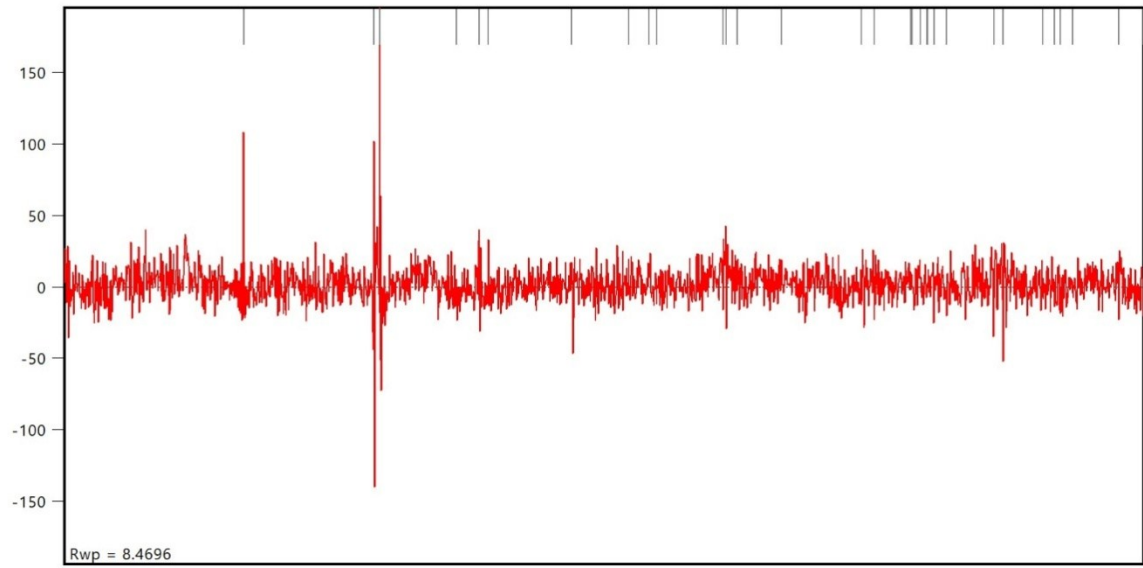
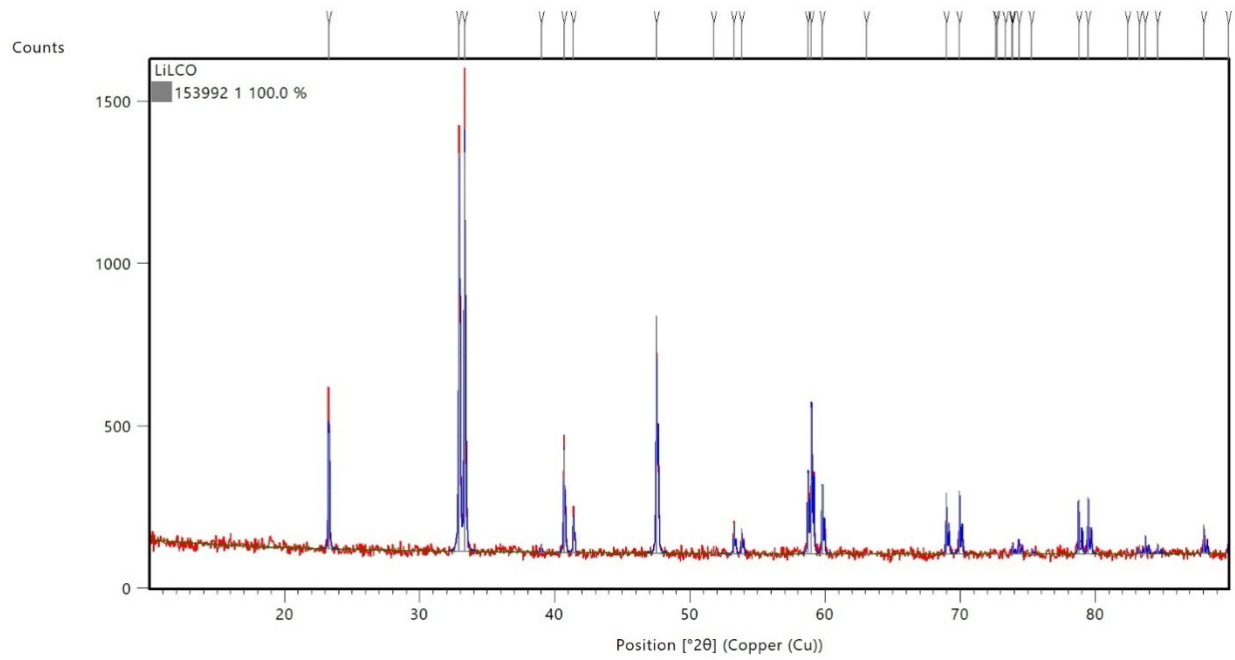


Fig.s4 Rietveld analysis of LLCO

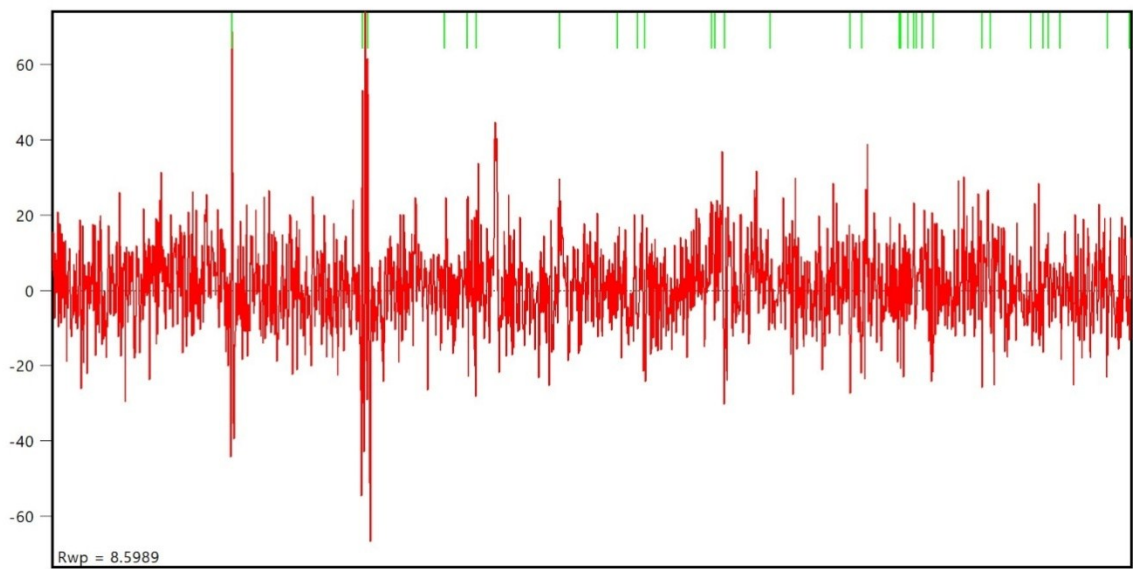
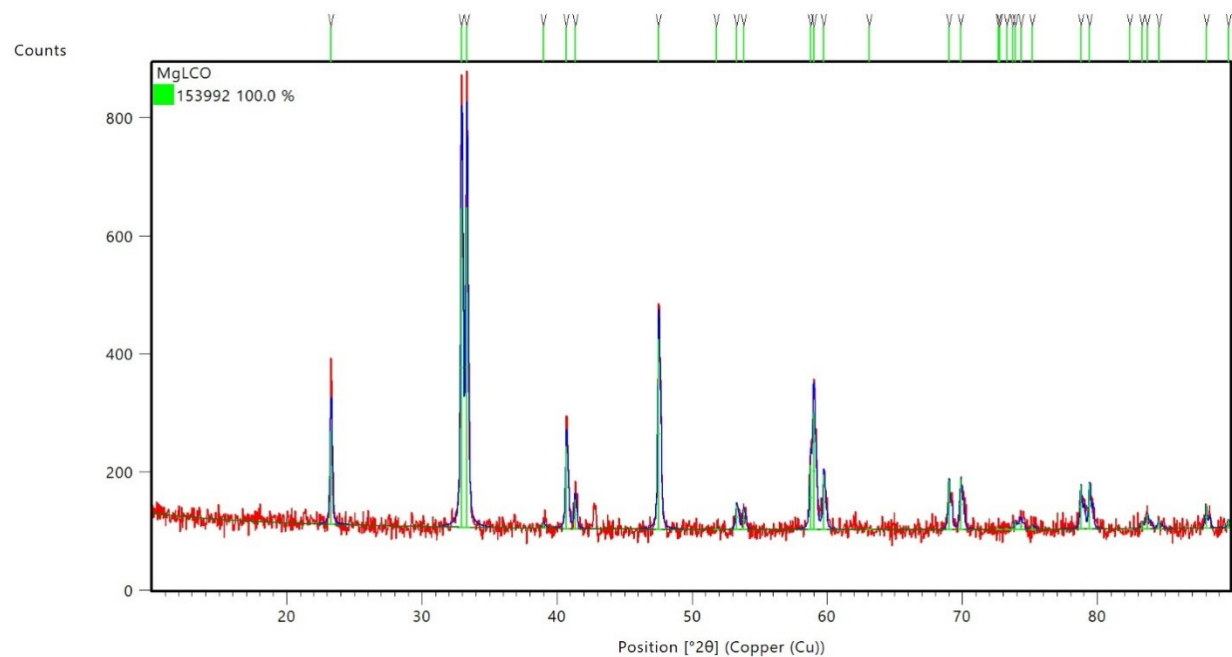


Fig.s5 Rietveld analysis of LMCO

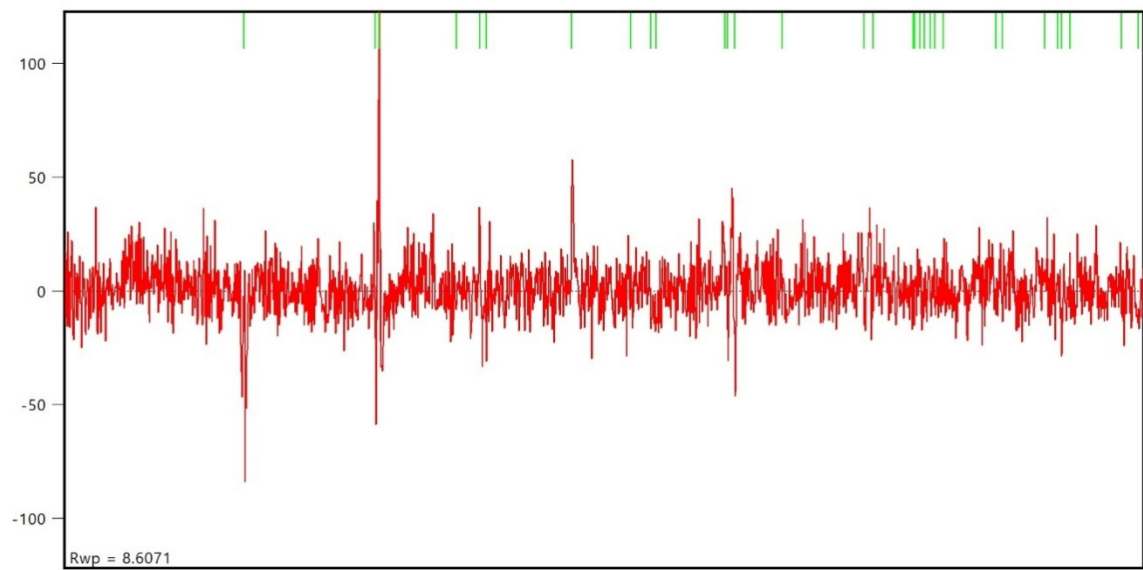
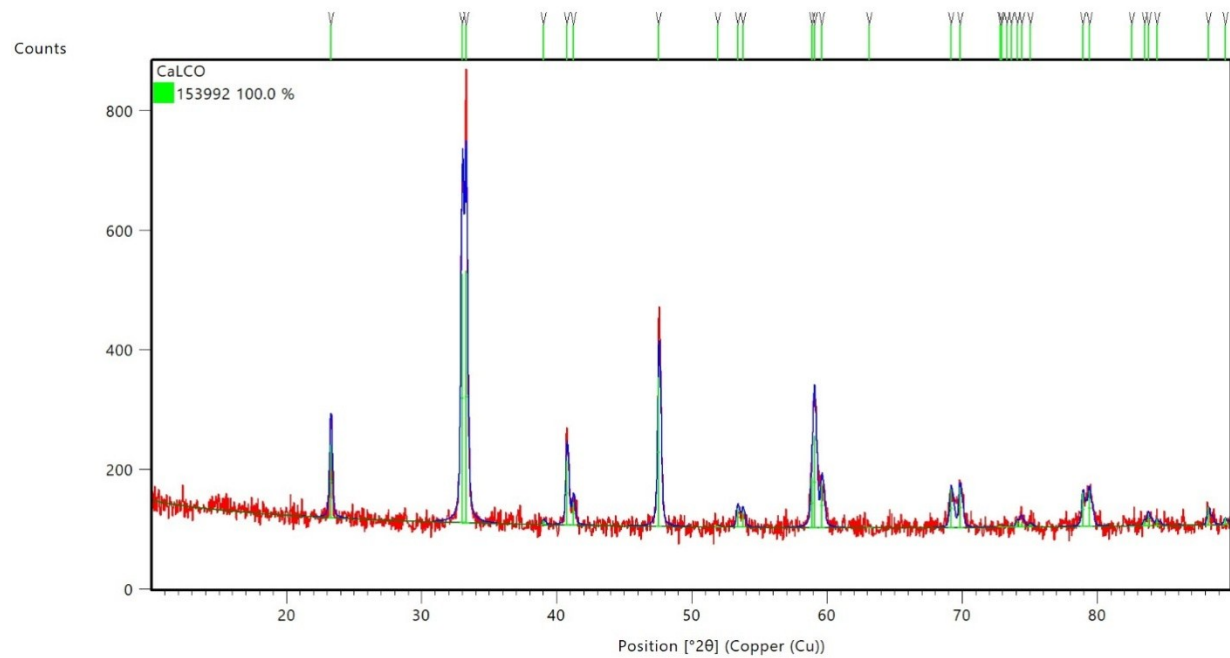


Fig.s6 Rietveld analysis of LCCO

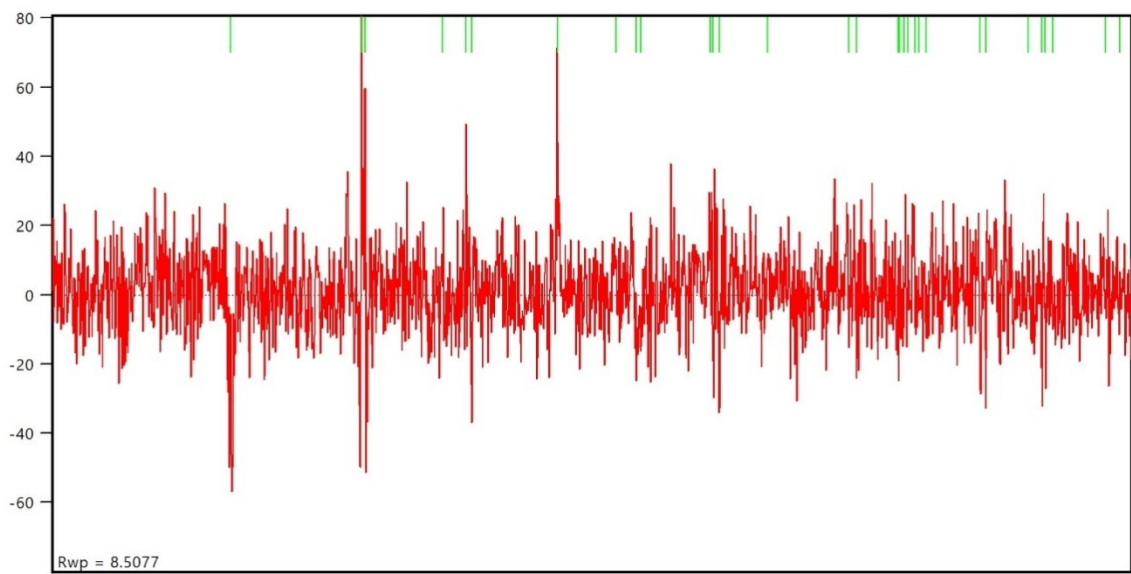
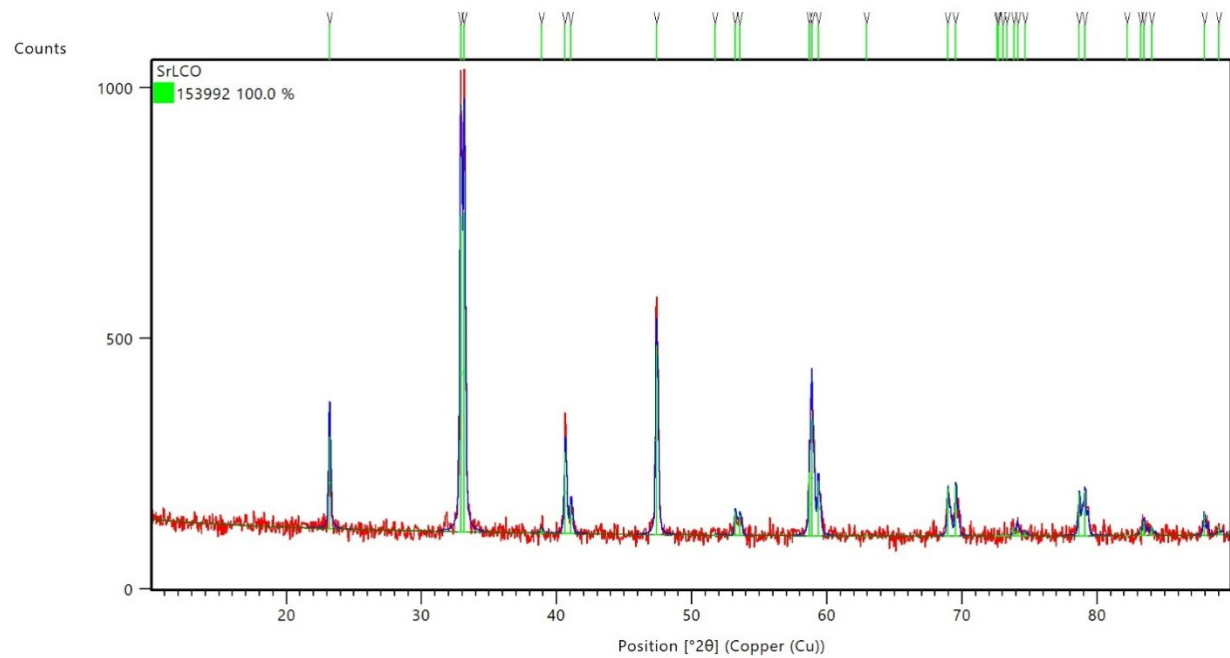


Fig.s7 Rietveld analysis of LSCO

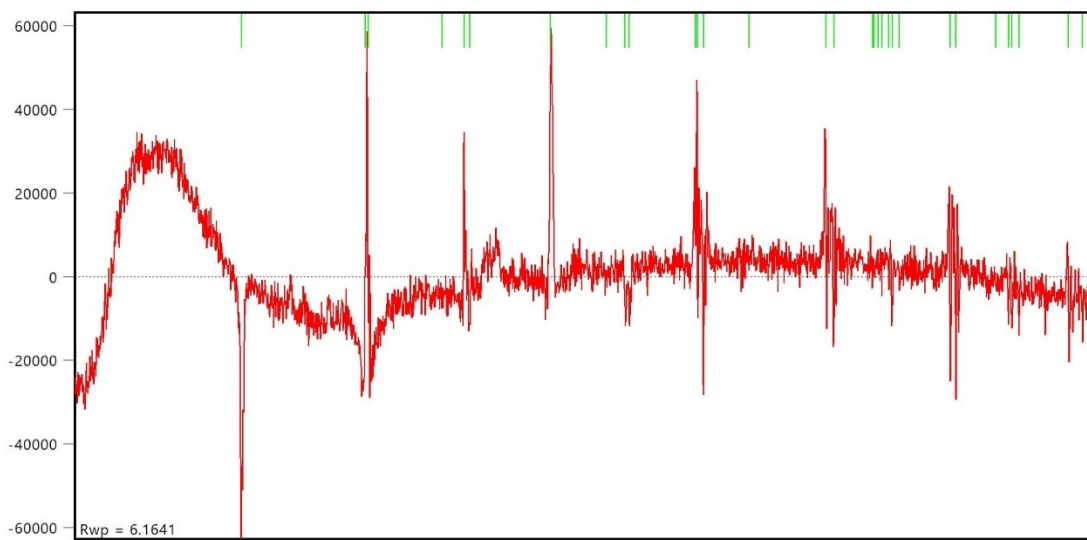
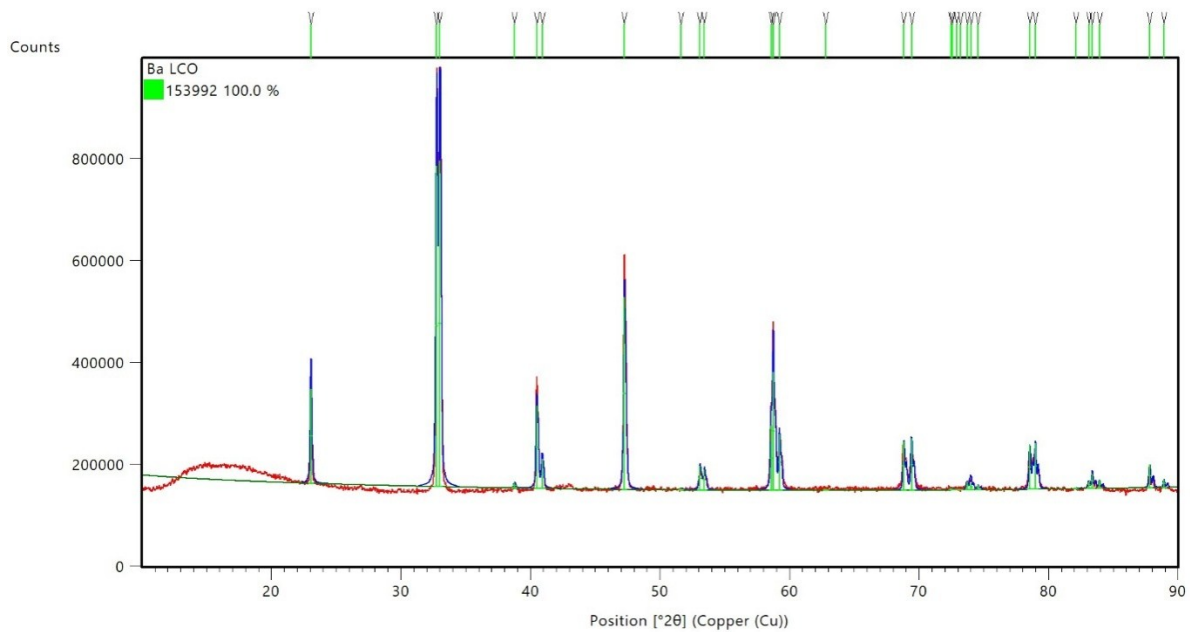


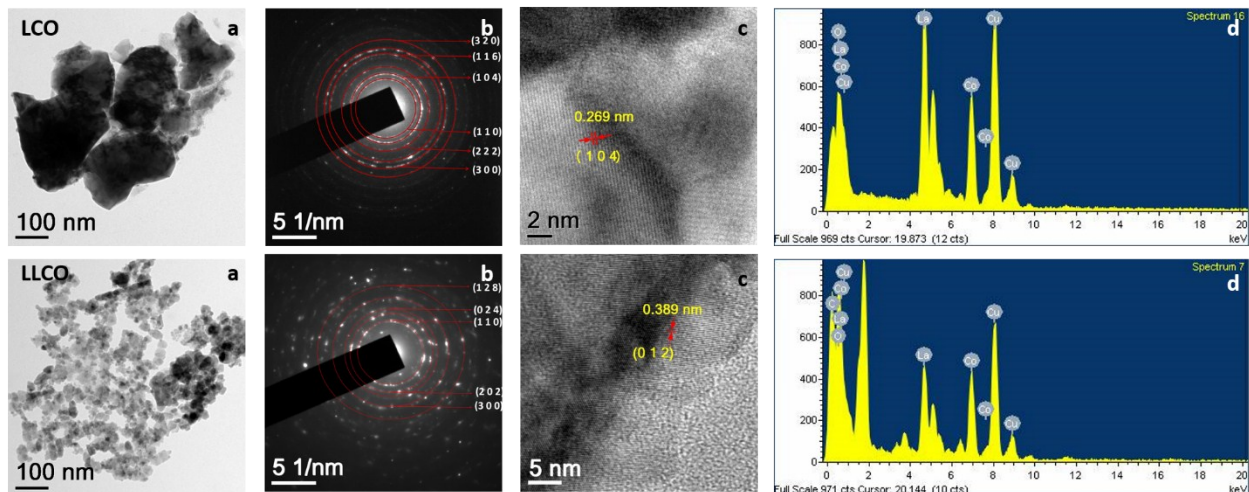
Fig.s

8 Rietveld analysis of LBCO

4. HRTEM analysis

The particle morphology of the prepared compounds were examined using High Resolution Transmission Electron Microscopic (HRTEM) analysis (JEOL JEM 2100) at an accelerating voltage of 200kV. Chemical analysis was performed by using OXFORD Energy dispersive X-ray spectrometer (EDS). The calcined nanoperovskites were initially ground, and a trace quantity was dispersed in ethanol which was subsequently sonicated for 3 min at 50 Hz. Later the nanoparticle solution was drop casted onto a carbon coated copper grid followed by drying before analyzing under TEM. Processed Selected Area Electron Diffraction (SAED) patterns were analyzed using the Digital micrograph software 1.85.1535 version.

HRTEM images of the calcined powder samples are shown in fig.s9. The images in fig.s9a show more uniform particle size distribution in LCCO, LLCO and LBCO when compared to the other doped perovskites. Concentric rings observed in all SAED patterns (fig.s9b) confirm the poly crystalline nature of the sample. Lattice fringes in the high resolution images (fig.s9c) confirm the single crystallinity of the individual particles. The diffraction rings in SAED patterns and interplanar spacing in HRTEM images can be indexed/interpreted based on the crystal structure obtained through the XRD data. EDS data in fig.s9d confirms the presence of parent and dopant elements and also absence of impurities.



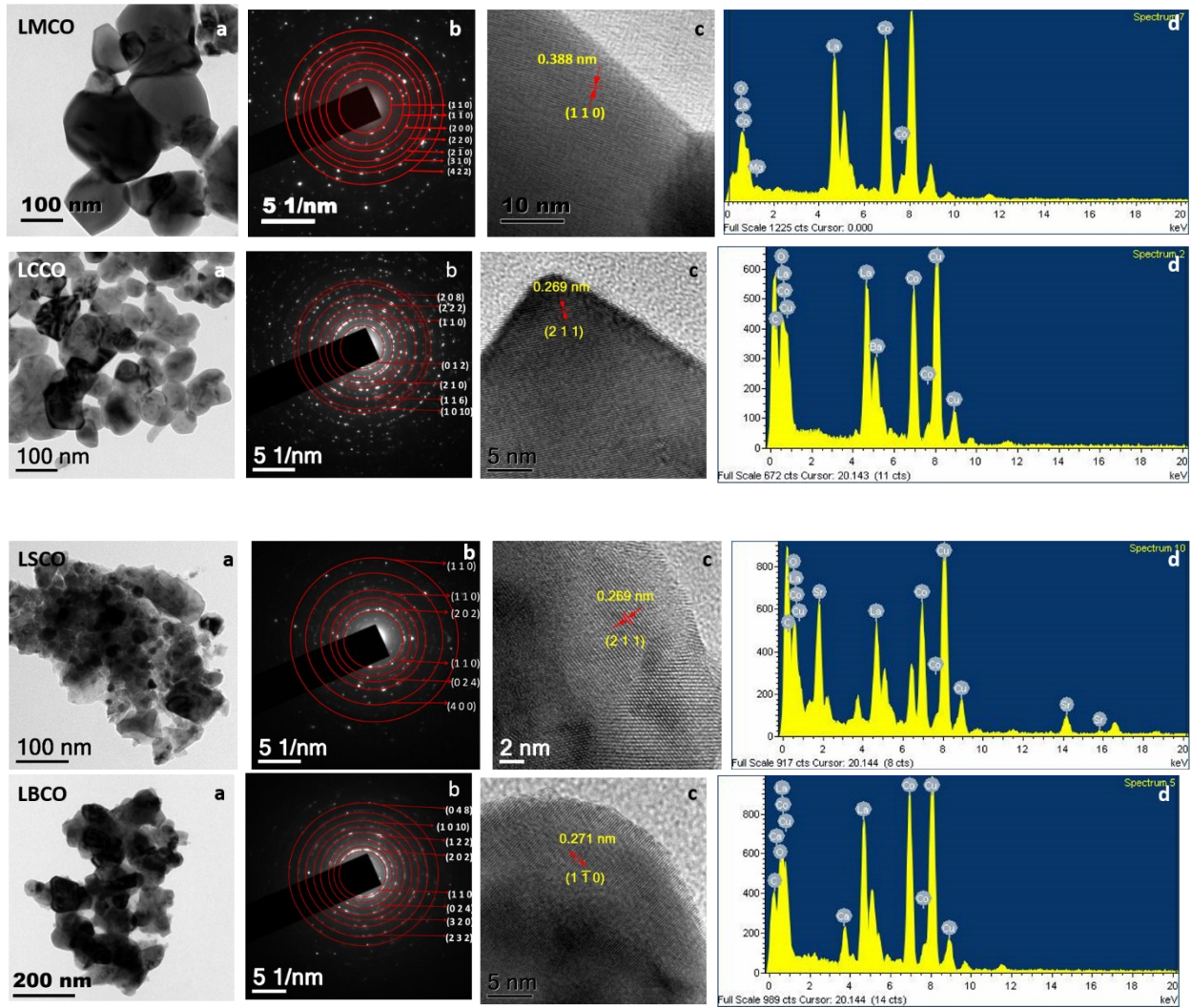


Fig.s9 HRTEM data of compounds (a) images revealing particle size, (b) SAED pattern, (c) High resolution image, (d) EDS

5. Grain size measurements using ImageJ software

Average grain size measured using Imagej software are 2376 nm, 2750 nm, 1125 nm, 1217 nm, 3471 nm, 971 nm for LCO, LLCO, LMCO, LCCO, LSCO and LBCO respectively(shown in fig.s10).

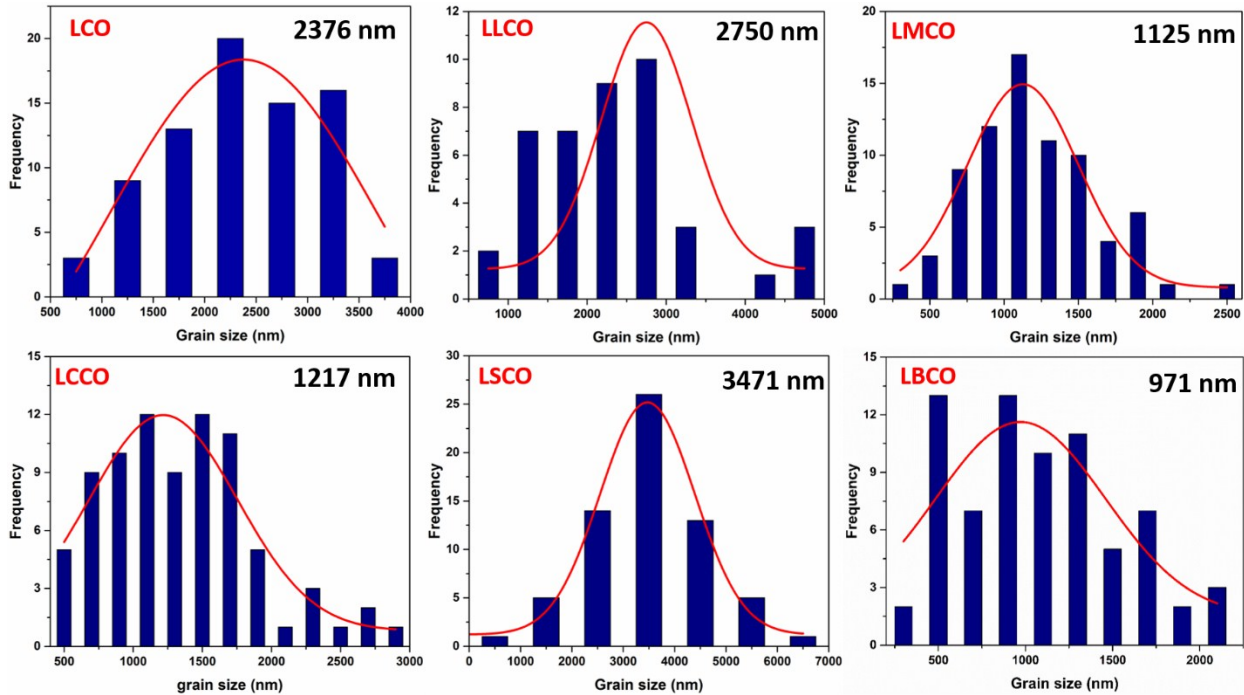


Fig.s10 Grain size measured by using imageJ software

6. Conductivity studies of materials

Table 4 shows the measured activation energy and temperature dependent electrical conductivity of the samples.

Table 4 Total conductivity and activation energy of the synthesized compounds

Compound	Total conductivity (σ_{total}) at various temperatures (S/cm)										Activation energy ΔE_a (eV)
	300° C	350° C	400° C	450° C	500° C	550° C	600° C	650° C	700° C	750° C	
LCO	8.88 E-08	3.21 E-07	1.14 E-06	2.72 E-06	6.04 E-06	1.14 E-05	2.07 E-05	3.70 E-05	6.93 E-05	1.15 E-04	0.799
LLCO	4.05 E-07	9.02 E-07	2.85 E-06	6.05 E-06	2.01 E-05	3.30 E-05	5.16 E-05	1.10 E-04	1.67 E-04	3.61 E-04	0.76
LMCO	1.13 E-07	3.74 E-07	1.34 E-06	3.38 E-06	8.34 E-06	1.54 E-05	3.62 E-05	7.25 E-05	1.29 E-04	2.10 E-04	0.85
LCCO	1.38 E-06	3.61 E-06	7.49 E-06	2.20 E-05	4.29 E-05	8.16 E-05	1.43 E-04	3.18 E-04	4.69 E-04	7.99 E-04	0.71
LSCO	2.16 E-07	5.77 E-07	1.49 E-06	4.02 E-06	9.40 E-06	1.92 E-05	3.36 E-05	6.37 E-05	1.30 E-04	2.06 E-04	0.82
LBCO	6.05	1.24	4.74	1.12	2.33	5.08	1.00	1.89	3.64	6.54	0.797

	E-07	E-06	E-06	E-05	E-05	E-05	E-04	E-04	E-04	E-04	
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