

## LIST OF FIGURES

**Fig. 1.1.** Ideal  $ABO_3$  perovskite unit cell depicting ‘A’ ions at (0, 0, 0), the ‘B’ ions (1/2, 1/2, 1/2) and ‘O’ ions at (0, 1/2, 1/2) positions in cubic lattice [7].

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**Fig. 1.3.** Different types of lattice arrangement resulting in different type (A-, C-, G- and E-type) antiferromagnetic ordering [11].

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**Fig. 1.12.** Phase diagram of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ , constructed from measurements of macroscopic quantities such as the resistivity and magnetic susceptibility, FM: Ferromagnetic Metal, FI: Ferromagnetic Insulator, AF: Antiferromagnetic, CAF: Canted AF, and CO: Charge/Orbital Ordered. FI and/or CAF could be spatially inhomogeneous states with FM and AF coexistence [32].

**Fig. 1.13.** Lower panel Lattice parameters and cell volume as a function of temperature for the  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  sample, measured on cooling. Lines through the points are guides to the eye. The shaded area represents the width of the magnetization hysteresis loop. Upper panel Magnetization ( $H = 1 \text{ T}$ ) and electric resistivity ( $H = 0 \text{ T}$ ) vs  $T$  for  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  measured on cooling [35].

**Fig. 1.14.** Variation of lattice parameters of bulk and nanocrystalline half doped  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  manganites with measuring temperature [37].

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**Fig. 1.23.** Temperature dependence of field cooled and zero field cooled susceptibility for (a) S30 (30 nm) and (b) S55 (55 nm). The measurements have been performed in the presence of 100 Oe magnetic field. Insets: a(i) and b(i). Temperature dependence of inverse zero field cooled susceptibility in high temperature region for S30 (30 nm) and S55 (55 nm), respectively. The temperature region above 300 K has been fitted according to the Curie–Weiss function,  $\chi \approx C/T - \theta_p$ . a(ii) and b(ii). The minima at temperature dependence of  $d\chi/dT$  indicated by arrow represent the paramagnetic to ferromagnetic transition [51].

**Fig. 1.24.** Variation of lattice parameters of NSMO1150 (bulk) and NSMO750 (nano) samples with temperature obtained from refinement of neutron diffraction data [53].

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**Fig. 1.29.** The temperature dependencies of magnetization (top), resistivity (middle) and lattice parameters (bottom) observed for bulk  $\text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  sample, ( $T_{CO} \approx 270$  K and  $T_N \approx 170$  K) [61].

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**Fig. 1.31.** M-H hysteresis loops at 4 K after FC under 10 kOe for the nanosized SCMO with different particle sizes. The inset shows the enlarged view of low field region [65].

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**Fig. 3.2.** X-ray photoelectron spectra (solid circles) of Mn  $2\text{P}_{3/2}$  core level for nanocrystalline  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  calcined at  $800^\circ\text{C}$ . The solid triangles and solid squares show the core level peak fits for the  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions, respectively. The

bottom curve (stars) shows Shirley background. The continuous line overlapping the observed XPS data (solid circles) shows the resulting curve fit [98].

**Fig. 3.3.** Experimentally observed (dots), Rietveld calculated (continuous line) and their difference (continuous bottom line) profiles for bulk and nanocrystalline  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  samples obtained after Rietveld analysis of the XRD data using orthorhombic space group *Pnma*. The vertical tick marks between the observed and difference plot show the Bragg peak positions [103].

**Fig. 3.4.** Experimentally observed (dots), Rietveld calculated (continuous line) and their difference (continuous bottom line) profiles for bulk and nanocrystalline  $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  samples obtained after Rietveld analysis of the XRD data using orthorhombic space group *Pnma*. The vertical tick marks between the observed and difference plot show the Bragg peak positions [104].

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**Fig. 3.6.** Evolution of the unit cell volume for bulk and nanocrystalline  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ ,  $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  and  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  samples calcined at various temperatures [108].

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**Fig. 3.8.** Evolution of lattice parameters for bulk and nanocrystalline samples calcined at various temperatures (a)  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  (b)  $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  and (c)  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  [111].

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**Fig. 3.11.** Magnetization (M) vs temperature (T) curve measured at 0.05 T and 1 T magnetic fields for (a) bulk  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  sample (lower panel) and nano  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  sample calcined at 800 °C (upper panel). Inset to figure (a) shows first order derivative of magnetization (M) with respect to temperature (T) for bulk  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  sample. Inset to figure (b) shows ac-susceptibility vs temperature for nanocrystalline  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  sample calcined at 800 °C [116].

**Fig. 3.12.** Magnetization (M) versus applied magnetic field (H) plot for bulk and nanocrystalline (calcined at 800 °C)  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  samples measured at 5 K (main panel) and at room temperature (RT) (inset). Ferromagnetic hysteresis loop is clearly seen for nano sample at 5 K. Inset shows the paramagnetic state for both the samples at 300 K (RT) [119].

**Fig. 3.13.** Magnetization (M) versus applied magnetic field (H) plot for nanocrystalline  $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  (left panel) and  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  (right panel) at 5 K. Ferromagnetic hysteresis loop is clearly seen for both the samples [119].

**Fig. 3.14.** Experimentally observed (dots), Rietveld calculated (continuous line) and their difference (continuous bottom line) profiles for nanocrystalline  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ ,

samples (prepared by Sol-Gel method and calcined at 700 °C) obtained after Rietveld analysis of the XRD data using orthorhombic space group Pnma. The vertical tick marks between the observed and difference plot show the Bragg peak positions. Upper panel at room temperature and lower panel at 15 K [121].

**Fig. 3.15.** Variation of unit cell volume (left upper panel) and lattice parameters (left lower panel) for  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  samples prepared by sol-gel method and calcined at various temperatures. The middle panel shows the evolution of strongest peak of  $\text{Mn}_3\text{O}_4$  impurity (around  $2\theta \approx 36.17$ ) for samples calcined at various temperatures. The samples calcined at 700, 800, 900, 1000, 1100 1300 °C are denoted as C7, C8, C9, C10, C11 and C13 respectively [124].

**Fig. 4.1.** Scanning electron microscopic (SEM) images of (a) bulk (C13) and (c) nano (C9)  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  samples. Energy dispersive Spectrum (EDS) of samples (b) C13 and (d) C9. Inset to Fig. 4.1(d) shows the TEM image of C9 samaple [133].

**Fig. 4.2.** X-ray photoelectron spectra (solid circles) of Mn  $2p_{3/2}$  core level for bulk (C13) and nano (C6)  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ . The solid triangles and solid squares show the core level peak fits for the  $\text{Mn}^{4+}$  and  $\text{Mn}^{3+}$  ions, respectively. The bottom curve (stars) shows Shirley background. The continuous line overlapping the observed XPS data (solid circles) shows the resulting curve fit [135].

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**Fig. 4.6.** Powder XRD patterns of  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  ceramics prepared at various calcination temperatures 600 °C, 700 °C, 800 °C, 900 °C, 1000 °C, 1100 °C, 1200 °C and 1300 °C. The strong superstructure peaks are marked by asterisks [144].

**Fig. 4.7.** Experimentally observed (dots), Rietveld calculated (continuous line) and their difference (continuous bottom line) profiles for bulk(C13)  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  at 300K obtained by using *Imma*. The vertical tick marks above difference plot show the Bragg peak positions [146].

**Fig. 4.8.** Evolution of selected XRD profiles with temperature (13 K to 300 K) for bulk (C13)  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  sample. The miller indices on top corresponding indexing using orthorhombic structure [147].

**Fig. 4.9.** Experimentally observed (dots), Rietveld calculated (continuous line) and their difference (continuous bottom line) profiles for bulk(C13)  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  at 13K obtained by using coexisting *Imma+P2<sub>1</sub>/m* space groups. The vertical tick marks above difference plot show the Bragg peak positions [150].

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**Fig. 4.13.** Experimentally observed (dots), Rietveld calculated (continuous line) and their difference (continuous bottom line) profiles for nanocrystalline (a) C9 and (b) C6  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  samples obtained after Le-Bail profile matching analysis of the XRD data. The vertical tick marks above the difference plot show the Bragg peak positions [159].

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**Fig. 5.2.** Powder XRD patterns of  $\text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  ceramics prepared at various calcination temperatures 600 °C, 700 °C, 800 °C, 900 °C, 1000 °C, 1100 °C, 1200 °C, 1300 °C and 1400 °C [166].

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*Pnma*. The vertical tick marks between the observed and difference plot show the Bragg peak positions [169].

**Fig. 5.5.** Experimentally observed (dots), Rietveld calculated (continuous line) and their difference (continuous bottom line) profiles for nanocrystalline  $\text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  samples (calcined at 1100 °C) obtained after Rietveld analysis of the XRD data using (a) orthorhombic space group *Pnma* and (b) coexistence of two phase with space group  $P2_1/m+Pnma$ . The vertical tick marks between the observed and difference plot show the Bragg peak positions [171].

**Fig. 5.6.** Experimentally observed (dots), Rietveld calculated (continuous line) and their difference (continuous bottom line) profiles for nanocrystalline  $\text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  samples (calcined at 900 °C) obtained after Le-Bail analysis of the XRD data using (a) coexistence of two phase with space group  $P2_1/m+Pnma$  (b) modulated crystal structure with monoclinic space group *Pm* with lattice parameters  $2a_o, b_o, 3c_o$ . The vertical tick marks between the observed and difference plot show the Bragg peak positions [172].

**Fig. 5.7.** Experimentally observed (dots), Rietveld calculated (continuous line) and their difference (continuous bottom line) profiles for nanocrystalline  $\text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  samples calcined at (700 °C) obtained after Le-Bail analysis of the XRD data using (a) modulated crystal structure with monoclinic space group *Pm* with lattice parameters  $2a_o, b_o, 3c_o$  and (b) modulated crystal structure with monoclinic space group *Pm* with lattice parameters  $5a_o, b_o, 2c_o$ . The vertical tick marks between the observed and difference plot show the Bragg peak positions [174].

**Fig. 5.8.** Variation of lattice parameters and unit cell volume with calcinations temperature/particle size for  $\text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  obtained by Le-Bail analysis of the structure. Lattice parameters and cell volume of modulated phases were suitably scaled to correspond to the orthorhombic cell parameter bulk sample [176].

**Fig. 5.9.** Magnetization vs temperature (M-T) plots for the  $\text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  samples are C7 (calcined at 700 °C), C9 (calcined at 900 °C) and C14 (calcined at 1400 °C) measured at the magnetic field of 0.05 T [178].

**Fig. 5.10.** Magnetization vs temperature (M-T) plots for the  $\text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  samples are C7 (calcined at 700 °C), C9 (calcined at 900 °C) and C14 (calcined at 1400 °C) measured at the magnetic field of 1 T [179].

**Fig. 5.11.** The Magnetization (M) vs applied magnetic field (H) plot for bulk and nanocrystalline  $\text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  measured at 5 K. Hysteresis indicative of ferromagnetism is clearly seen [181].