Chapter: V

Emergence of two New Modulated Phases and Suppression of Charge Ordering Transition in Nanocrystalline $Sm_{0.5}Ca_{0.5}MnO_3$ Ceramic

Chapter-V

5.1 Introduction

In previous chapter, we have shown that reduction of crystallite size in nanocrystalline $Nd_{0.5}Sr_{0.5}MnO_3$ leads to emergence of a new modulated monoclinic phase. In this chapter, we have shown that nanocrystalline samples of $Sm_{0.5}Ca_{0.5}MnO_3$ (SCMO) exhibit two new modulated monoclinic phases in *Pm* space group. As discussed in chapter I, the structure of bulk SCMO at room temperature is orthorhombic in the Pnma space group. We will show in this chapter that reduction of crystallite size to nanometer scale not only results into emergence of two new modulated phases but also coexistence of orthorhombic and low temperature monoclinic ($P2_1/m$ space group) phases for a particular range of crystallite size. As will be discussed in subsequent sections, nanocrystalline SCMO sample calcined at 1100 ^oC show coexistence of orthorhombic (*Pnma*) and monoclinic ($P2_1/m$) phases which is normally observed at low temperatures in bulk samples. This chapter also presents the result of our investigation on magnetic phase transition on bulk and nanocrystalline $Sm_{0.5}Ca_{0.5}MnO_3$ samples of different crystallite sizes below room temperature. The magnetic characterization of the nano samples reveals the suppressed charge ordering.

5.2 Experimental Details

Details of sample synthesis are already described in chapter II. The phase purity and crystal structures of the samples were studies by 18 kW rotating Cu anode Rigaku powder diffractometer operating in the Bragg–Brentano geometry and fitted with a graphite monochromator in the diffracted beam. The data were collected in the 2θ

range 15°–120° at scan step of 0.02°. The XRD data were analyzed by Rietveld structure refinement and Le-Bail full profile matching methods using FULLPROF suite [Carvajal 2011]. In the refinements, pseudo-Voigt function was used to define peak shape and sixth coefficient polynomial was used to generate the background. We have also used the micro structural strain parameters during structure refinement of $Sm_{0.5}Ca_{0.5}MnO_3$ samples. Magnetic characterizations were carried out as described in chapter II.

5.3 Results and Discussions

5.3.1 Microstructure Analysis

Fig. 5.1 shows the SEM micrograph of nanocrystalline $Sm_{0.5}Ca_{0.5}MnO_3$ samples calcined at 700 ^oC and 900 ^oC. As can be seen from these figures, the microstructure has uniform morphology and the particle size is smaller for calcination temperature of 700 ^oC in comparison to 900 ^oC. The average particle sizes for samples calcined at 700 ^oC and 900 ^oC was determined to be ~25 nm and ~100 nm respectively. The crystallite sizes of the samples were also determined by XRD using Scherer formula and Rietveld method. The crystallite sizes of the samples calcined at temperatures 600, 700, 800, 900, 1000, 1100, 1200 and 1300 ^0C were obtained to be 25.29, 37.96, 40.63, 44.66, 89.92, 339.93, 420.07 and 450.25 nm respectively using Rietveld method. The crystallite sizes determined from various methods were found to be in well agreement.

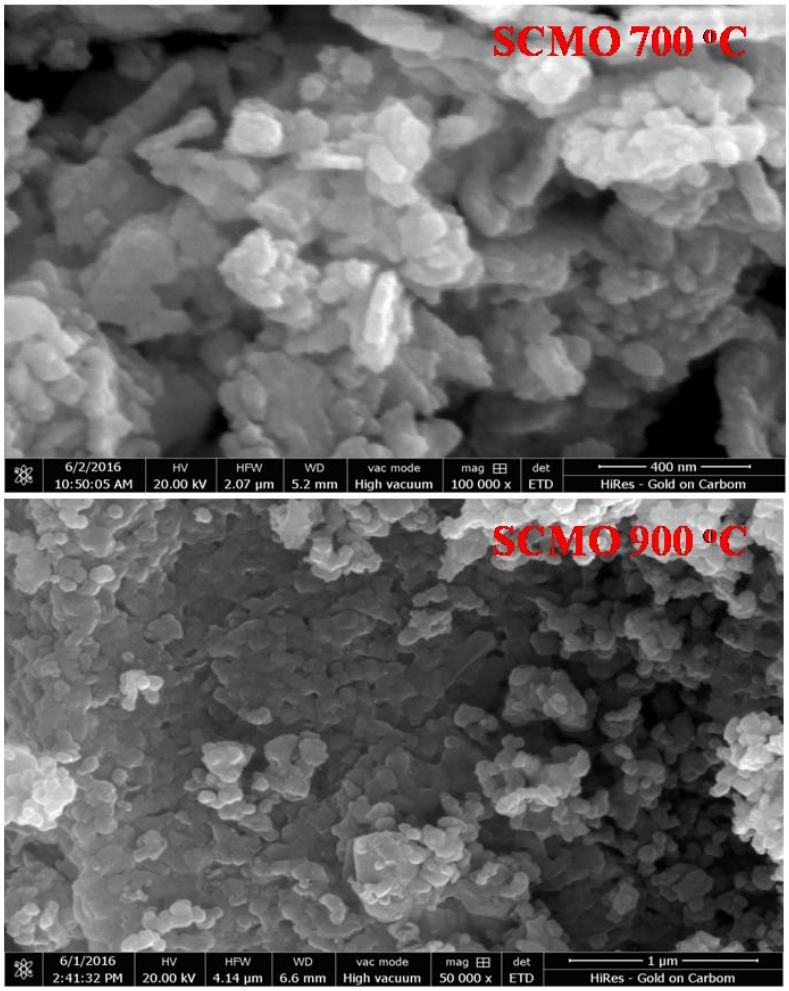

Fig. 5.1. The scanning electron microscope (SEM) images of $Sm_{0.5}Ca_{0.5}MnO_3$ ceramics prepared at calcinations temperautre 700 ^oC and 900 ^oC.

5.3.2 Structural Analysis

Fig.5.2. shows the room temperature x-ray diffraction patterns of $Sm_{0.5}Ca_{0.5}MnO_3$ samples calcined at various temperatures viz. 700, 800, 900, 1000, 1100, 1200, 1300 and 1400 ^oC with various crystallite sizes. As can be seen from this figure, the perovskite phase is obtained for all the samples. As will be confirmed in the subsequent section, the bulk sample calcined at 1400 ^oC can be indexed by considering orthorhombic structure in the Pnma space group in well agreement with the reports of earlier authors [Tomioka et al. (1997), Tokura et al. (2006), Zhou et al. (2008)]. It is evident from Fig.5.2 that with decreasing calcination temperature and crystallite size several new reflections appear in addition to those observed for the orthorhombic Pnma structure. Some of the reflections which appear or disappear with changing calcination temperature/crystallite size are marked by letter 'M' and asterisks in Fig.5.2. A careful examination of the evolution of week superlattice reflections in Fig.5.2 suggests that the structure of this compound is very sensitive to the calcination temperature/crystallite size. We have carried out the Rietveld analysis of the XRD patterns of these samples considering different plausible structural models to determine the correct structures for samples calcined at various temperatures. Rietveld analysis of the structure for samples of various crystallite sizes reveals that there are four crystallographic structures which appear with changing crystallite size/calcination temperature.

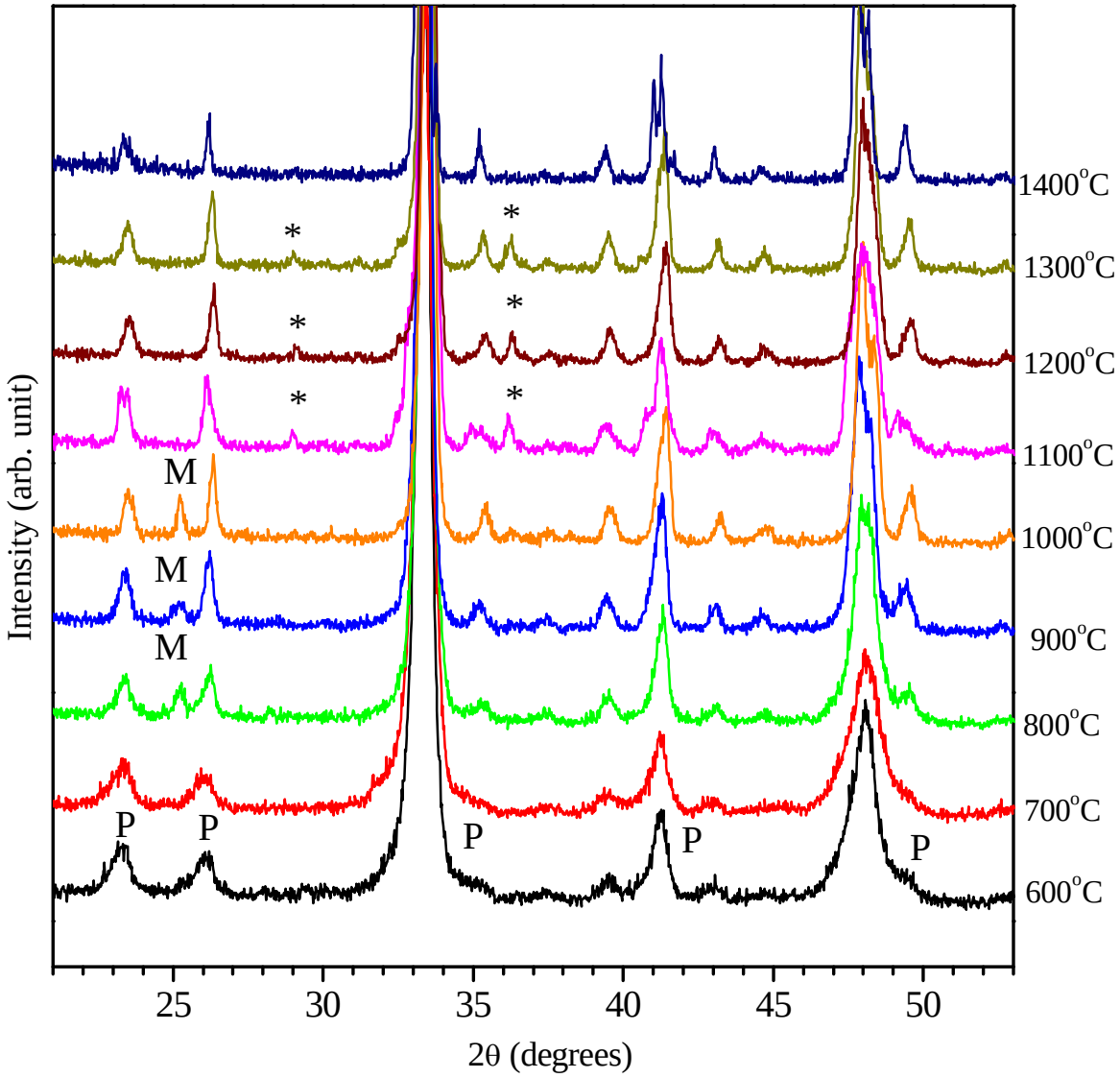

Fig. 5.2. Powder XRD patterns of $Sm_{0.5}Ca_{0.5}MnO_3$ ceramics prepared at various calcination temperatures 600 °C, 700 °C, 800 °C, 900 °C, 1000 °C, 1100 °C, 1200 °C, 1300 °C and 1400 °C.

To illustrate it further, we show in Fig. 5.3, evolution of selected XRD profiles of four representative samples corresponding to the four crystalline phases. The sample calcined at 1400 ^{o}C exhibit bulk orthorhombic structure in the *Pnma* space group. The samples calcined at 700 ^{o}C and 1000 ^{o}C show two different types of lattice modulations as is evident from the appearance of superlattice reflections in the XRD patterns. As will be shown in section 5.3.2.2 the sample calcined at 1100 ^{o}C exhibit two coexisting crystallographic phases.

5.3.2.1 Rietveld Refinement of the Structure of Bulk Samples

The structure of SCMO in bulk form is reported to be orthorhombic in the Pnma space group by earlier workers [Tokura et al. (1999)]. Rietveld refinement of the structure of the sample calcined at 1400 ^{o}C, 1300 ^{o}C and 1200 ^{o}C confirms that these samples exhibit orthorhombic structure in the *Pnma* space group. A very good fit between experimentally observed and Rietveld calculated XRD profiles for the sample calcined at 1400 ^{o}C using orthorhombic structure in the *Pnma* space group is shown in Fig.5.4. Refined lattice parameters were obtained to be a = 5.399(3), b = 7.547(4) and c = 5.351(3), which is in well agreement with the earlier reports [Tokura et al 2006].

5.3.2.2 Rietveld Refinement of the Structure of Sample Calcined at 1100 ^{o}C

Rietveld refinement of the structure of the sample calcined at 1100 ^{o}C using orthorhombic structure in the Pnma space group shows significant mismatch in the observed and calculated XRD profiles and higher χ^2 value (see top panel of Fig.5.3).

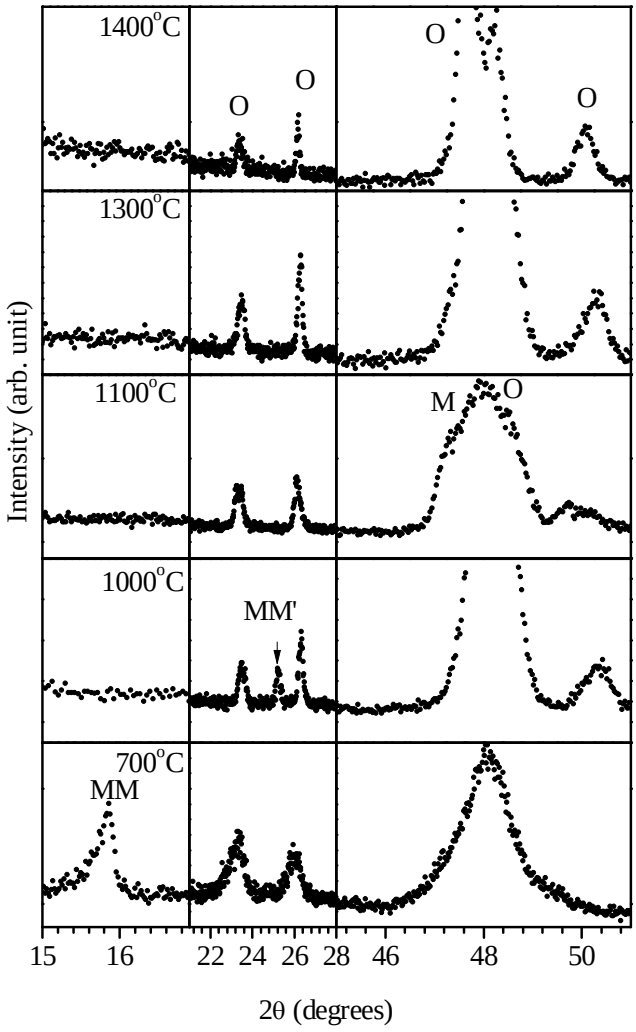

Fig.5.3. Evolution of selected XRD profiles with calcinations temperature for $Sm_{0.5}Ca_{0.5}MnO_3$ samples.

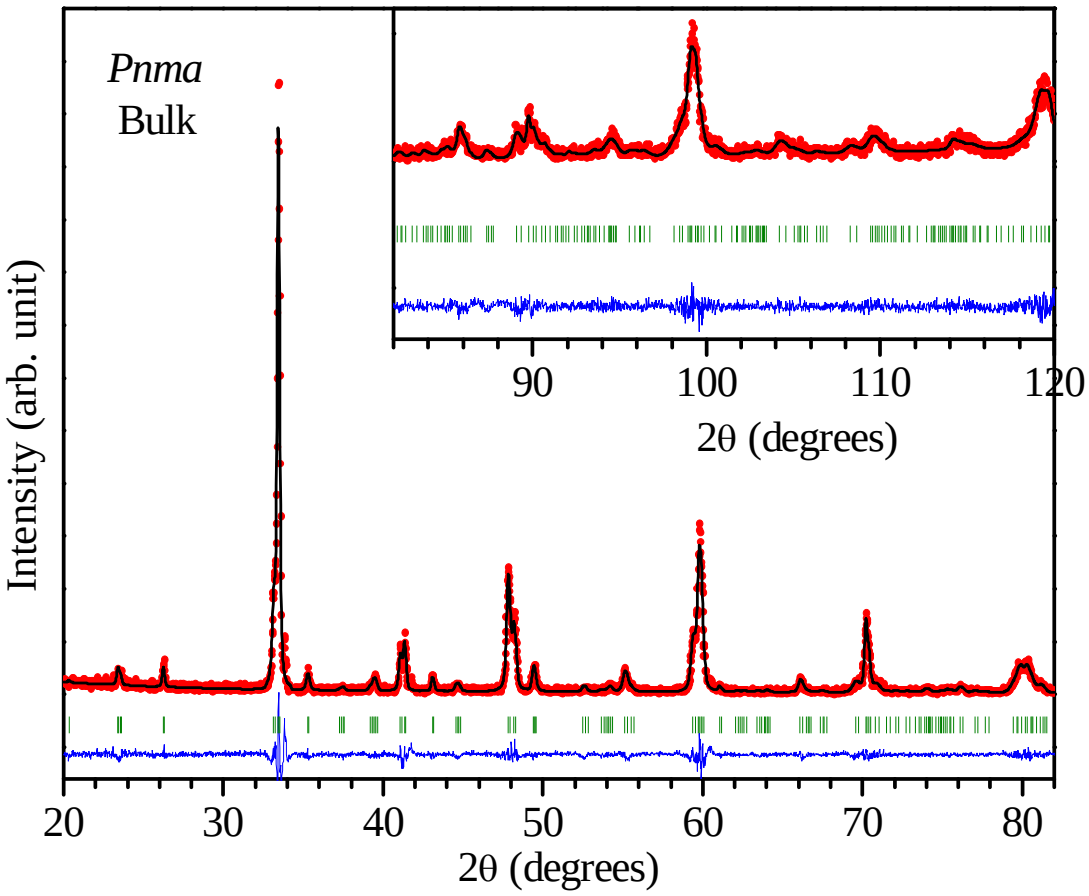

Fig. 5.4. Experimentally observed (dots), Rietveld calculated (continuous line) and their difference (continuous bottom line) profiles for bulk $Sm_{0.5}Ca_{0.5}MnO_3$, samples obtained after Rietveld analysis of the XRD data using orthorhombic space group *Pnma*. The vertical tick marks between the observed and difference plot show the Bragg peak positions.

We considered various plausible structural models to refine the structure of this sample which reveals that the structure of this sample exhibit two coexisting phases in the Pnma and $P2_1/m$ space group. Such a phase coexistence is observed below room temperature in bulk samples of several half doped manganites like LCMO [Radaelli et al. (1995); Radaelli et al. (1997)], NSMO [Kuwahara et al. (1995); Lopez et al. (2001)] and SCMO [Tokura et al. (1999)] etc. Appearance of low temperature phase at room temperature may be attributed to the reduction of crystallite size. A very good fit between experimentally observed and Rietveld calculated XRD profiles for the sample calcined at 1100 ^oC using coexisting orthorhombic (*Pnma*) and monoclinic ($P2_1/m$) structures is shown in Fig.5.5 (Lower panel).

5.3.2.3 Rietveld refinement of the Structure of sample Calcined at 900 ^oC

Similar to the sample calcined at 1100 ^oC, we tried to refine the structure of the samples calcined at 1000 ^oC and 900 ^oC using coexisting orthorhombic (*Pnma*) and monoclinic ($P2_1/m$) structures. However, this structural model could not account for the observed XRD profiles. There are several additional superlattice reflections which are left unindexed from this structural model as shown in Fig.5.6(a) (see inset). In view of this we considered modulated monoclinic structures similar to that discussed in previous chapter and used for explaining the structure of nanocrystalline $Nd_{0.5}Sr_{0.5}MnO_3$. Fig.5.6(b) shows that Rietveld refinement fit for the nanocrystalline $Sm_{0.5}Ca_{0.5}MnO_3$ sample calcined at 900 ^0C using monoclinic Pm space group and a modulated unit cell with cell parameters ~$2a_o$, ~b_o, ~$3c_o$, where a_o, b_o, c_o correspond to the cell parameters of the orthorhombic cell in the *Pnma* space group for the bulk

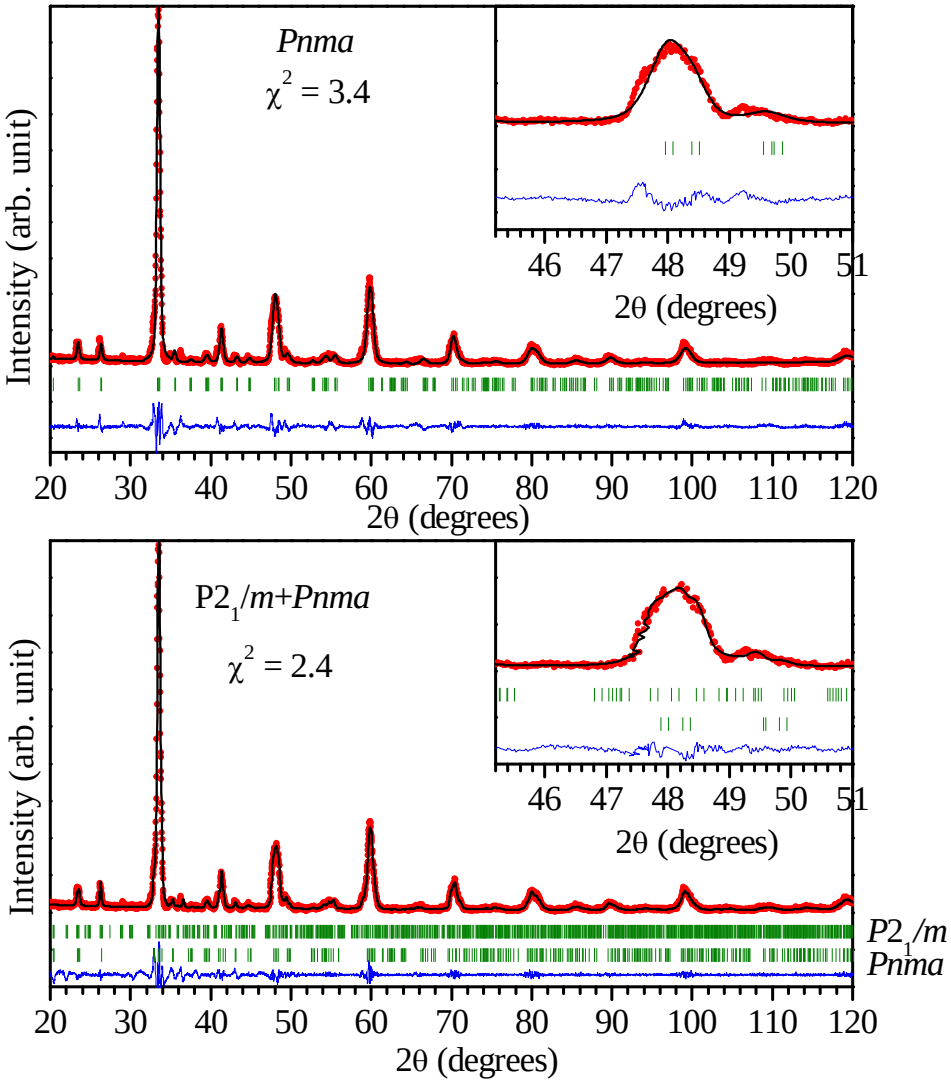

Fig. 5.5. Experimentally observed (dots), Rietveld calculated (continuous line) and their difference (continuous bottom line) profiles for nanocrystalline $Sm_{0.5}Ca_{0.5}MnO_3$, samples (calcined at 1100 ^oC) obtained after Rietveld analysis of the XRD data using (a) orthorhombic space group *Pnma* 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.

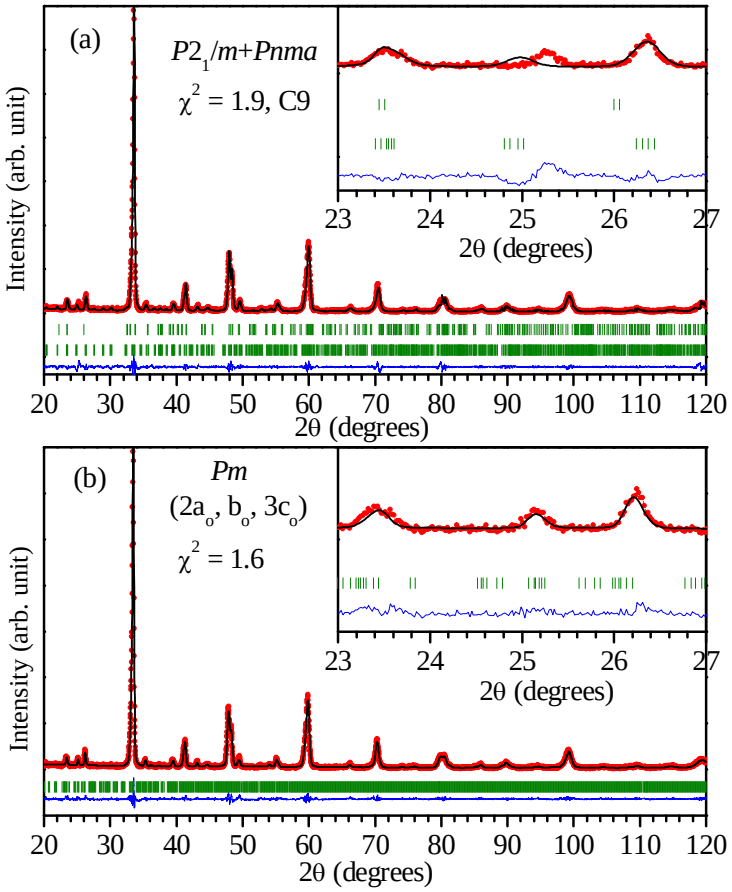

Fig. 5.6. Experimentally observed (dots), Rietveld calculated (continuous line) and their difference (continuous bottom line) profiles for nanocrystalline $Sm_{0.5}Ca_{0.5}MnO_3$, samples (calcined at 900 ^oC) obtained after Le-Bail analysis of the XRD data using (a) coexistence of two phase with space 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.

SCMO sample. As can be seen from Fig.5.6(b), a very good fit between observed and calculated profiles are obtained for this structure. This confirms that the structure of the nanocrystalline SCMO samples calcined at 900 ^{o}C and 1000 ^{o}C is similar to the nanocrystalline $Nd_{0.5}Sr_{0.5}MnO_3$ samples. The refined lattice parameter for SCMO sample calcined at 900 ^{o}C is obtained to be a = 10.8839 Å, b = 7.6815 Å, c = 16.2896 Å and β = 90.607. Thus decreasing the crystallite size modifies the structure of SCMO from orthorhombic *Pnma* to monoclinic Pm with twofold modulation in the unit cell along a_o, threefold along c_o, while b_o remains unchanged.

5.3.2.4 Rietveld refinement of the Structure of sample Calcined at 700 ^{o}C

Rietveld refinement of the structure of the samples calcined at further lower temperatures (800 ^{o}C and 700 ^{o}C) with smaller crystallite sizes, using modulated Pm phase used above could not explain the observed XRD profiles. As shown in Fig. 5.7(a) there are some additional superlattice reflections left unindexed (see inset to figure), which were not present in the samples prepared at higher temperatures. A new superlattice reflection appears at significantly lower two-theta value (15.8), for the samples calcined at 700^{o}C and 800 ^{o}C, which requires larger unit cell modulations. In view of this we considered different combinations of unit cell modulations using monoclinic *Pm* space group. A rigorous analysis of the structure considering various possibilities reveals that the observed XRD pattern could be fitted well by considering a modulated monoclinic structure in the Pm space group with unit cell parameters ~$5a_o$, ~b_o, ~$2c_o$, where a_o, b_o, c_o correspond to the cell parameters of the orthorhombic cell in the *Pnma* space group for the bulk SCMO sample.

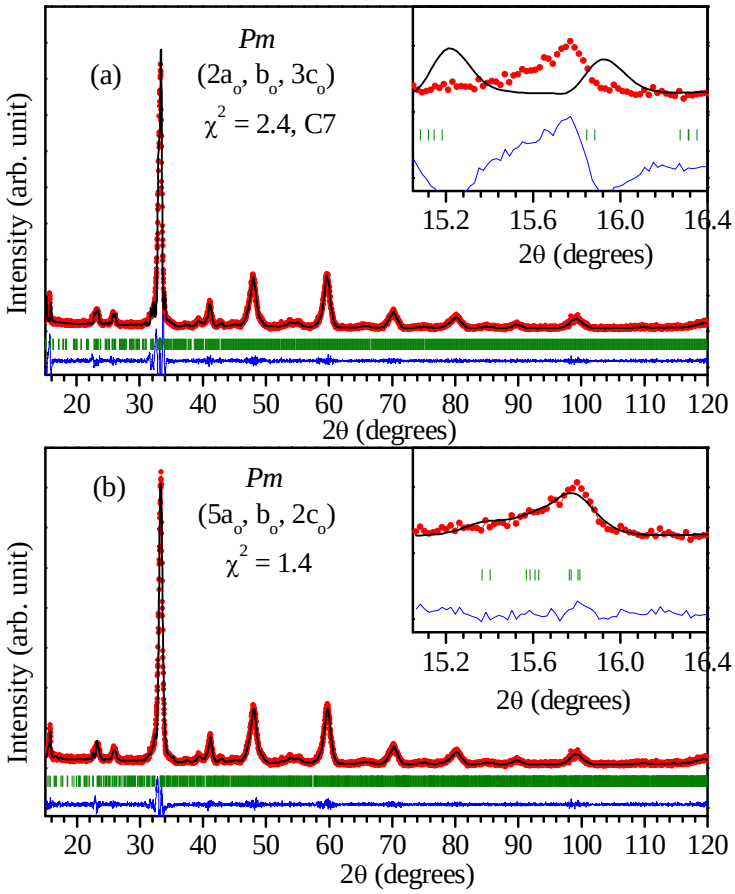

Fig. 5.7. Experimentally observed (dots), Rietveld calculated (continuous line) and their difference (continuous bottom line) profiles for nanocrystalline $Sm_{0.5}Ca_{0.5}MnO_3$, samples calcined at (700 ^oC) obtained after Le-Bail analysis of the XRD data using (a) modulated crystal structure with 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.

A very good fit between observed and calculated profiles using this structural model for the SCMO samples calcined at 700 ^{o}C is shown in Fig.5.7(b). Inset to Fig.5.7(b) illustrates the good quality of fit for superlattice reflection arising due to the structural modulation. The refined lattice parameters for the SCMO sample calcined at 700 ^{o}C is obtained to be a = 26.7482 Å, b = 7.5489 Å, c = 10.7904 Å and β = 90. 081. Thus the nanocrystalline SCMO samples exhibit two types of modulated monoclinic structures depending upon the crystallite size in contrast to nanocrystalline $Nd_{0.5}Sr_{0.5}MnO_3$ samples where only on modulated phase is observed.

5.3.2.5 Variation of unit Cell Parameters with Calcination temperature

Fig. 5.8 shows the variation of cell parameters and unit cell volume with calcination temperature. The cell parameters and unit cell volumes of the modulated phases were suitably scaled to correspond to the orthorhombic unit cell parameters for plotting in Fig.5.8, to have one to one correspondence. As can be seen from Fig.5.8, there is little variation in the cell parameters for modulated phases while changing crystallite size. The lattice parameters of the bulk samples in the orthorhombic structure also show insignificant change with changing calcination temperature. However, a discontinuous change is observed in the cell parameter for the samples calcined at 1000 ^{o}C and 1100 ^{o}C, where transition from the modulated monoclinic structure to the bulk orthorhombic structure (*Pnma* space group) takes place. The unit cell volume also changes discontinuously around this transition.

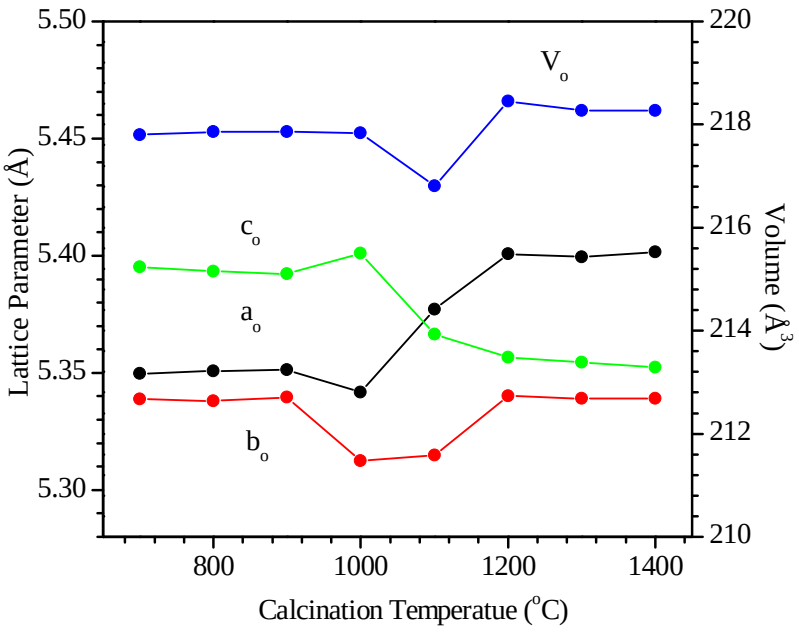

Fig. 5.8. Variation of lattice parameters and unit cell volume with calcinations temperature/particle size for $Sm_{0.5}Ca_{0.5}MnO_3$ obtained by Le-Bail analysis of the structure. Lattice parameters and cell volume of modulated phases were suitably scaled to correspond to the orthorhombic cell parameter bulk sample.

5.3.3 Magnetic Phase Transitions in SCMO samples below room temperature

Figs. 5.9 and 5.10, shows the temperature dependences of the zero-field cooled (ZFC), field cooled cooling (FCC) and field cooled warming (FCW), magnetization data measured under a magnetic field 0.05T and 1T respectively, for the nano (calcined at 700 and 900 ^{o}C) and bulk (calcined at 1400 ^{o}C). As depicted in the insets to the Figs. 5.9 and 5.10, the anomaly in the magnetization at charge ordering transition temperature (T_{CO}) is clearly seen around 280 K for bulk samples but it is not present in the nanocrystalline samples calcined at 700 ^{o}C. This anomaly becomes quite weaker for the nano sample calcined at 900 ^{o}C, suggesting that reduction of the crystallite size is weakening the charge ordered phase in SCMO sample. Similar behaviour in M(T) data has been reported for bulk and nanocrystalline samples of SCMO by earlier authors also [Zhou et al. (2008), Giri et al. (2014)]. Thus the charge ordering transition in nanocrystalline SCMO is suppressed similar that observed for the nanocrystalline LCMO, and NSMO samples discussed in earlier chapters. A bifurcation in the temperature dependent magnetization data is seen for the ZFC and FCC measurements corresponding to the magnetic glass transition temperatures in these samples which is consistent with the earlier reports [Zhou et al. (2008), Giri et al. (2014)].

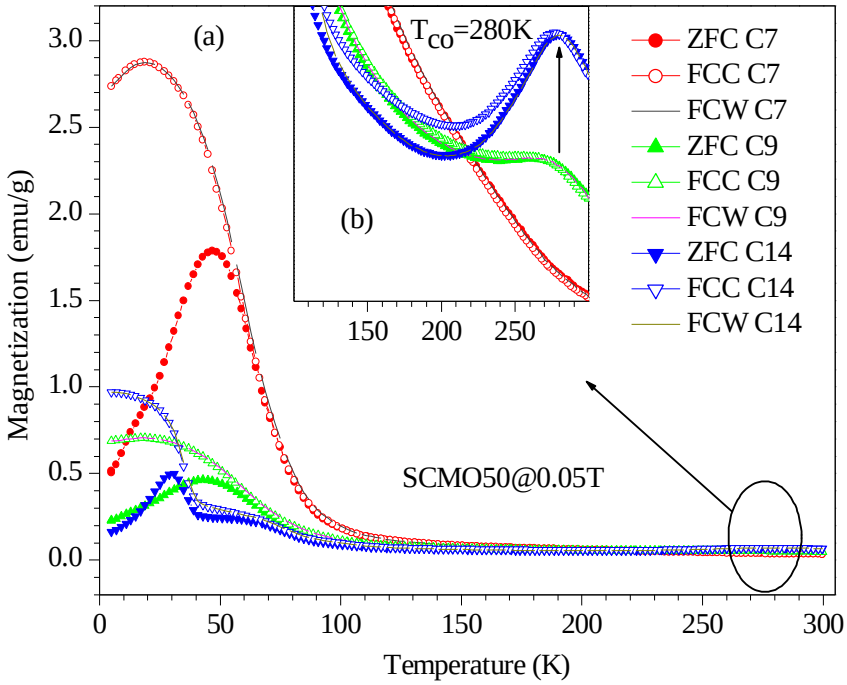

Fig. 5.9. Magnetization vs temperature (M-T) plots for the $Sm_{0.5}Ca_{0.5}MnO_3$ samples are C7 (calcined at 700 ^{0}C), C9 (calcined at 900 ^{0}C) and C14 (calcined at 1400 ^{0}C) measured at the magnetic field of 0.05 T.

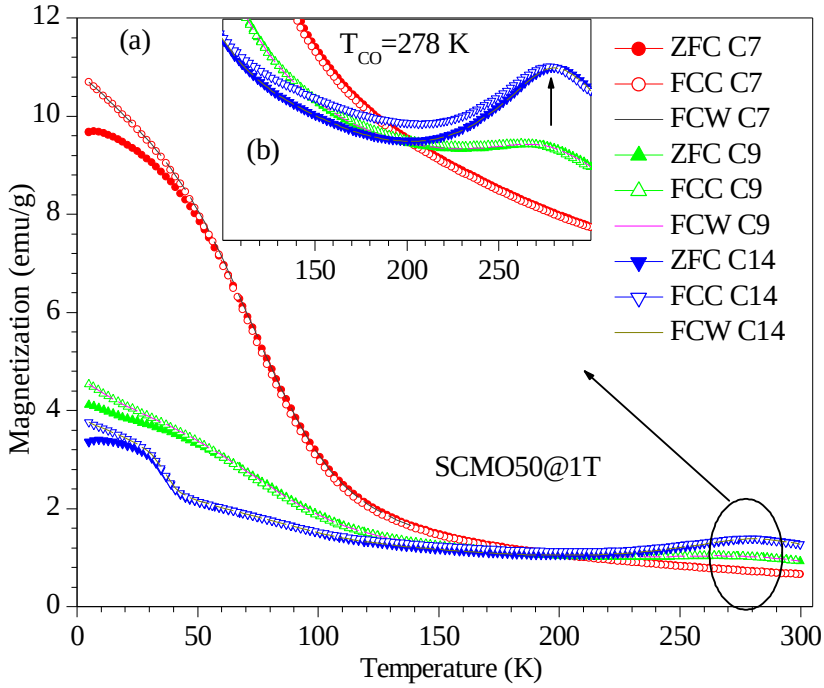

Fig. 5.10. Magnetization vs temperature (M-T) plots for the $Sm_{0.5}Ca_{0.5}MnO_3$ samples are C7 (calcined at 700 ^{0}C), C9 (calcined at 900 ^{0}C) and C14 (calcined at 1400 ^{0}C) measured at the magnetic field of 1 T.

Fig. 5.11 shows the magnetization (M)-magnetic field (H) hysteresis measurement data for bulk (calcined at 1400 ^{o}C) and nano (calcined at 700 and 900 ^{o}C) samples recorded at 5K. As can be seen from this figure a clear M-H loop expected for the ferromagnetic state is observed for the nano sample calcined at 700 ^{o}C. With increasing calcination temperature, the M-H loop becomes slim due to weakening of the ferromagnetic order and appearance of the charge ordering transition and antiferromagnetic character. The observed M-H loops for bulk and nano samples are in well agreement with the earlier reports [Zhou et al. (2008), Giri et al. (2014)]. However, in contrast to earlier reports, we have discovered new modulated phases in the nanocrystalline SCMO samples which missed the attention of earlier authors.

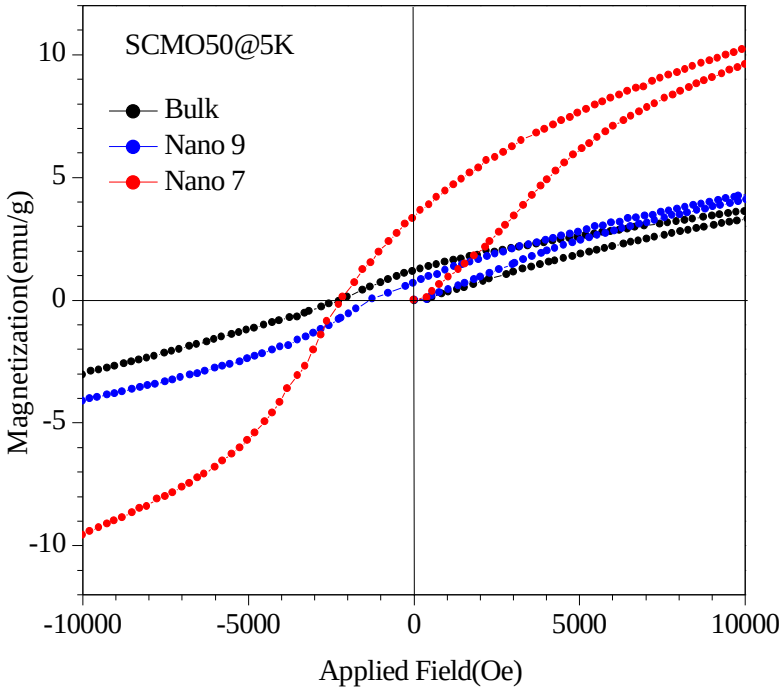

Fig. 5.11. The Magnetization (M) vs applied magnetic field (H) plot for bulk and nanocrystalline $Sm_{0.5}Ca_{0.5}MnO_3$ measured at 5K. Hysteresis indicative of ferromagnetism is clearly seen .

5.4 Summary

We have discovered two new modulated monoclinic phases in nanocrystalline $Sm_{0.5}Ca_{0.5}MnO_3$ ceramics. The nano samples calcined at 700 ^oC and 800 ^oC exhibit monoclinic Pm space group with a modulated unit cell parameters ~$5a_o$, ~b_o, ~$2c_o$ while the samples calcined at 900 ^oC and 1000 ^oC exhibit monoclinic Pm space group with a modulated unit cell parameters ~$2a_o$, ~b_o, ~$3c_o$, where a_o, b_o, c_o correspond to the cell parameters of the orthorhombic cell in the *Pnma* space group for the bulk SCMO sample. The SCMO sample calcined at 1100 ^0C shows coexistence of monoclinic (space group $P2_1/m$) and orthorhombic (space group *Pnma*) structures. The SCMO samples calcined at 1200 ^0C, 1300 ^0C and 1400 ^0C exhibit bulk orthorhombic structure in the *Pnma* space group. The magnetic characterizations of the SCMO samples reveal suppression of charge ordering transition in nanocrystalline samples.