Study of A-site disorder dependent structural properties and magnetic ordering in polycrystalline perovskite Sm$_{0.5}$Ca$_{0.5-x}$Sr$_x$MnO$_3$

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Abstract
This paper reports the studies on the effect of A-site substitution by strontium on the structural properties and magnetic ordering in polycrystalline perovskite Sm$_{0.5}$Ca$_{0.5-x}$Sr$_x$MnO$_3$ ($x = 0.1, 0.2$ and $0.3$). The investigated samples are prepared by conventional solid-state reaction technique. XRD analysis at room temperature has confirmed orthorhombic structure of the sample with space group Pnma. The dependence of structural parameter, Curie temperature and coercivity on Sr doping content has been thoroughly investigated. It is observed that substitution of Sr$^{2+}$ for Ca$^{2+}$ increases lattice parameter, tolerance factor and the Curie temperature. However, the coercivity ($H_c$) decreases with increasing Sr content while the charge ordering process is weakened with increasing Sr content. Field cooled (FC) and zero-field cooled (ZFC) dc magnetizations measurements at low field and low temperature indicate that there is a spin-glass (SG) like state occurred. Temperature dependent ac susceptibility at different frequency indicates a spin-glass-like transition of the sample.

Introduction:
The alkaline doped rare-earth manganites, RE$_{1-x}$AE$_x$MnO$_3$ (RE = rare earth and AE = alkaline-earth element) have been studied extensively as they show interesting properties like metal insulator transition, colossal magnetoresistance (CMR) and magnetocaloric effect [1–3]. These compounds also show a higher electrical resistivity, which is favorable for reducing eddy current heating [4]. In these manganites, a decrease in the average ionic radii of the RE$^{3+}$ and AE$^{2+}$ cations, generally leads to an increase in tilting of MnO$_6$ octahedral or the Mn–O–Mn bond angle [5]. As a result ferromagnetic (FM) state is relatively destabilized in a distorted perovskite manganite. In such a case, a FM state is frequently replaced by an anti-ferromagnetic (AFM) insulator with Charge/orbital ordering (CO/OO) [6]. Sm$_{0.5}$Sr$_{0.5}$MnO$_3$ shows ferromagnetic metallic behavior and Sm$_{0.5}$Ca$_{0.5}$MnO$_3$ behaves like an antiferromagnetic charge/orbital ordered insulator. Our goal is to investigate the competing features between FM and CO/OO with Sr content in Sm$_{0.5}$Ca$_{0.5-x}$Sr$_x$MnO$_3$.

Experimental:
Polycrystalline samples of Sm$_{0.5}$Ca$_{0.5-x}$Sr$_x$MnO$_3$ ($x = 0.1, 0.2$ and $0.3$) were prepared by conventional solid-state reaction technique. High purity oxides and carbonates (MnCO$_3$, Sm$_2$O$_3$, SrCO$_3$, and CaCO$_3$) were weighed in stoichiometric proportion and mixed thoroughly by hand in an agate mortar and pestle. The mixed sample was then ball milled in a planetary ball mill for 6 h and then calcined at 800 °C. The calcined samples were sintered at 850 °C, 900 °C, 950 °C, 980 °C, 1020 °C and 1050 °C temperature each for 12 h with intermediate grounding and pelletizing. Structural characterizations were done by X-ray diffraction (XRD) technique (Geol. Diffractometer) and structural parameters were extracted using a commercial software. Microstructure and
chemical composition were determined by using Scanning Electron Microscopy (SEM) which includes an energy dispersive x-ray diffractometer (EDX). Field cooled (FC) and zero field cooled (ZFC) magnetization, magnetization as a function of magnetic field at different temperatures and temperature dependent ac susceptibility $M'(T)$ were investigated by means of a Quantum Design Superconducting Quantum Interference Device (SQUID) magnetometer.

Results and discussion:

Room temperature XRD patterns of $\text{Sm}_{0.5}\text{Ca}_{0.5-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.1, 0.2$ and $0.3$) are shown in figure 1(a). Detailed analysis (those related to the phase characterization and identification of diffraction reflections) of the crystal structure based on reference code # 04-018-9809 in X’pert Highscore Plus software with jcpds reveals that all the samples are found to be crystallized in orthorhombic system and all the peaks are related to Pnma space group. But the Miller indices of only the major peaks are shown in the figure 1(a). The shift of the XRD peaks towards smaller angles demonstrates an increase of the lattice parameters in the prepared samples with increase in Sr content. Also, it is clearly seen that all the samples are single phase in nature without any detectable impurities within the measurement range of study. All patterns share the same characteristics peaks and there are no anomalous peaks due to impurities.

The lattice parameters $a$, $b$ and $c$ as well as the cell volume $V$ are calculated from the XRD data analyzed with Rietveld refinement using an ‘X’pert Highscore Plus’ software and summarized in table 1. It is observed that cell volume increases due to the substitution of Ca$^{2+}$ ($r_a \sim 1.18$ Å) by a larger Sr$^{2+}$ ion ($r_a \sim 1.32$ Å). However, no structural phase transition has been found in the system. The lattice parameters $a$, $b$ and $c/\sqrt{2}$ verified the relation $c/\sqrt{2} < a < b$ which indicates that the samples are characterized by the presence of static Jahn–Teller distortion [7]. In perovskite manganites, the Jahn–Teller (JT) effect plays an important role in ground state (GS) and transport properties. Where, in this system three electrons in Mn ion lie in lower $t_{2g}$ levels, contributing a
| x  | System       | Space group | a (Å) | b (Å)  | c (Å) | $c/\sqrt{2}$ | $\alpha = \beta = \gamma$ | Cell volume (Å³) | Tolerance factor (t) | Grain size, (D) (nm) | Crystallite size (d) (nm) |
|----|--------------|-------------|------|-------|------|-------------|------------------|-----------------|---------------------|----------------------|-----------------------|
| 0.1| Orthorhombic | Pnma        | 5.378| 5.398 | 7.568| 5.35        | 90°              | 219.704         | 0.856               | 349                  | 28.0                  |
| 0.2| Orthorhombic | Pnma        | 5.385| 5.397 | 7.602| 5.37        | 90°              | 220.91          | 0.864               | 352                  | 34.2                  |
| 0.3| Orthorhombic | Pnma        | 5.394| 5.402 | 7.618| 3.87        | 90°              | 221.97          | 0.870               | 364                  | 41.8                  |
orthorhombic structure

Where, in a perovskite structure and deformation from an ideal cubic perovskite structure, is calculated from the ionic radii of the lattice sites. The tolerance factor which is a measure of deviation from an ideal cubic perovskite structure, is calculated from the ionic radii of the lattice sites in a perovskite structure and defined by Goldschmidt as

\[ t = \frac{\langle r_A \rangle + r_O}{\sqrt{2} (\langle r_{Mn} \rangle + r_O)} \]

Where \( \langle r_A \rangle \), \( \langle r_{Mn} \rangle \) and \( r_O \) are the average ionic radius of the A-site, Mn and O ions respectively. The average A-site ionic radius for our sample is calculated using

\[ \langle r_A \rangle = 0.5 \langle r_{Sm^{3+}} \rangle + (1 - x) \langle r_{Ca^{2+}} \rangle + x \langle r_{Sr^{2+}} \rangle. \]

As \( t \) decreases from 1, the lattice structure transforms to rhombohedral \( (0.96 < t < 1) \) and then to orthorhombic structure \( (t < 0.96) \) [9]. For our samples the tolerance factor \( t \) varies from 0.856 for \( x = 0.1 \) to 0.870 for \( x = 0.3 \) (table 1). This is attributed essentially to the replacement of a smaller \( Ca^{2+} \) ion by a larger ion of \( Sr^{2+} \).

The XRD profiles of the samples in figure 1(a) indicate a decrease in the width of diffraction peaks with increasing \( x \), resulting in an increase in crystallite size. The crystallite sizes \( d \) are evaluated from the XRD profiles of the samples using Debye- Scherer equation

\[ d = \frac{K\lambda}{\beta \cos \theta} \]

Where,

- \( d \) = Crystallite size (nm)
- \( K \) = 0.9 (Scherer constant)
- \( \lambda \) = 0.15406 nm (wavelength of the x-ray)
- \( \beta \) = FWHM (radians)
- \( \theta \) = Peak position (radians)

X'pert HighScore Plus software was used to evaluate 2\( \theta \) and FWHM values from the XRD profiles of the samples and Microsoft Excel software was used to calculate the \( d \) value using Debye- Scherer equation. A regular enhancement in crystallite sizes \( d \) is seen in the samples with increase in \( x \) content. The tolerance factor which is a measure of deviation from an ideal cubic perovskite structure, is calculated from the ionic radii of the lattice sites in a perovskite structure and defined by Goldschmidt as

\[ t = \frac{\langle r_A \rangle + r_O}{\sqrt{2} (\langle r_{Mn} \rangle + r_O)} \]

The EDX spectrum shows some impurity element like Ba (0.4%) and C (0.3%) as shown in figure 1(c) which has been considered negligible within experimental error. Then the elemental composition of the synthesized samples normalized to 100 wt% is given in table 2 which shows that the calculated value agreed well with the experimental value.

Figure 1(b) shows SEM image of a representative sample with \( x = 0.3 \). It is seen that the sample contains small and larger size particles homogeneously distributed throughout the sample. The average grain sizes \( D \) are estimated from SEM images by using 'Image' software with line intercept method. In this method

\[ \text{Average grain size} = \frac{\text{Line length}}{\text{No of grain}} \]

In this way average grain size was measured as many times as possible and their mean value was taken as final average grain size. The \( D \) values for all the samples are larger in comparison to their crystallite size, indicating a multi-domain structure [10]. Figure 1(c) shows the EDX spectrum of a representative sample with \( x = 0.3 \). The EDX spectrum shows some impurity element like Ba (0.4%) and C (0.3%) as shown in figure 1(c) which has been considered negligible within experimental error. Then the elemental composition of the synthesized samples normalized to 100 wt% is given in table 2 which shows that the calculated value agreed well with the experimental value.

Figure 2(a) shows zero-field cooled (ZFC) and field cooled (FC) magnetization measured at 100 Oe applied field from temperature 10 K to 150 K and inset shows the temperature range 150 K to 300 K. Field cooled (FC) and zero-field cooled (ZFC) DC magnetization measurements show a divergence at low temperature, which indicates the coexistence of anti-ferromagnetic and ferromagnetic clusters. Some salient features of these curves are that all the samples exhibit a paramagnetic to ferromagnetic transition and the Curie temperature increased with increasing \( x \), resulting in an increase in crystallite size. The crystallite sizes \( d \) is seen in the samples with increase in \( x \) content. The tolerance factor which is a measure of deviation from an ideal cubic perovskite structure, is calculated from the ionic radii of the lattice sites in a perovskite structure and defined by Goldschmidt as

\[ t = \frac{\langle r_A \rangle + r_O}{\sqrt{2} (\langle r_{Mn} \rangle + r_O)} \]

As \( t \) decreases from 1, the lattice structure transforms to rhombohedral \( (0.96 < t < 1) \) and then to orthorhombic structure \( (t < 0.96) \) [9]. For our samples the tolerance factor \( t \) varies from 0.856 for \( x = 0.1 \) to 0.870 for \( x = 0.3 \) (table 1). This is attributed essentially to the replacement of a smaller \( Ca^{2+} \) ion by a larger ion of \( Sr^{2+} \).

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inset of figure 2(a) and indicates the charge ordering temperature ($T_{\text{CO}}$). The sample with $x = 0.1$ shows a clear charge ordering at temperature $T_{\text{CO}} = 225$ K. For $x = 0.2$ the broad hump is almost disappeared and for $x = 0.3$ the charge ordering process is weakened and the observed $T_{\text{CO}} = 211$ K.

In ZFC curve for $x = 0.1$ a broad hump is seen around $T = 225$ K due to charge ordering and another kink is found around 110 K (more visible in dM/dT versus T curves) which correspond to antiferromagnetic ordering. With further lowering the temperature magnetic moments of larger size particle tend to align and magnetization increases around 50 K. The magnetization decreases onward due to the relaxation of magnetic moments of the larger size particles and it continues up to temperature 30 K. Upon further lowering of temperature magnetization increases presumably due to the magnetic moment ordering of smaller size particle until the temperature reaches up to 21 K. Afterwards the magnetization decreases due to relaxation of smaller size particles. From the extrapolation of these curves from their peaks it is seen that relaxation of small size particles occur more rapidly than that of large size particles. The ZFC curves for other samples shows the similar trend but the amount of magnetization increases and the Curie temperatures shifted to higher temperature with increasing Sr content. Curie temperature is determined from the minimum of the dM/dT versus T curves which has been shown in figure 1(b). It is found that $T_c$ increases with increasing Sr content from 22 K for $x = 0.1$ to 31 K for $x = 0.3$.

In figure 5(b), the isothermal M–H curves at temperature $T = 100$ K show a linear behavior which indicates the antiferromagnetic state. The enlarged figure at very low field is shown in the inset of figure 3(b) which shows some coercivity ($H_c$) for $x = 0.1$ and $x = 0.3$ but coercivity ($H_c$) for $x = 0.2$ is found approximately zero. At M–H curves at $T = 10$ K, the situation is changed slightly as shown in the figure 3(a), the behavior of the samples is still dominated by paramagnetic contributions and saturation is not reached in fields up to 50,000 Oe (5 T) applied field. The enlarged figure at very low field is included in the inset of figure 3(a) which shows that coercivity ($H_c$) decreases from 1238 Oe to 308 Oe with increasing Sr content. These values of coercivity ($H_c$) reveal the characteristics of short-range FM order in Sm$_{0.6}$Ca$_{0.5-x}$Sr$_x$MnO$_3$. It is also seen from the lower inset of figure 3(a) that hysteresis loop for the sample with $x = 0.2$ is shifted toward the negative field which is a signature of exchange bias effect that happens due to the ferro and anti-ferromagnetic coupling.

Temperature dependent inverse magnetic susceptibility ($1/\chi = H/M$) curves (shown in figure 4(a)) deduced from M(T) measurement in a magnetic field of 100 Oe show a clear deviation from the mean-field Curie–Weiss behavior above $T_C$ [13]. The degree of magnetic frustration can be measured by the divergence

Table 2. Table for elemental composition of Sm$_{0.5}$Ca$_{0.5-x}$Sr$_x$MnO$_3$ in weight % and number of atom from EDX measurement.

| $x$ | Weight % | Number of atom |
|-----|----------|----------------|
| 0.1 | 35.62    | 0.48           |
| 0.2 | 34.90    | 0.48           |
| 0.3 | 34.18    | 0.48           |
|     |          |                |
| 0.1 | 34.90    | 0.48           |
| 0.2 | 34.18    | 0.48           |
| 0.3 | 34.90    | 0.48           |

Figure 2. (a) Temperature dependent field cooled (FC) and zero field cooled (ZFC) magnetization curves at $H = 100$ Oe from temperature 10 K to 150 K and inset shows the temperature range 150 K to 300 K for Sm$_{0.5}$Ca$_{0.5-x}$Sr$_x$MnO$_3$. (b) temperature derivative of M(T) curves taken at 100 Oe and inset shows dM/dT versus T curves from 100 K to 300 K.
between $T_c$ and $\theta$, where $\theta$ is the paramagnetic Curie temperature. In our case the $\theta$ value are higher than the $T_c$ value. This difference between the experimental and theoretical data confirms the magnetic inhomogeneity of the sample around $T_c$. In order to understand the spin glass (SG) behavior a frequency dependent ac susceptibility $\chi'(T)$ measurement at low field was done. In figure 4(b) the ac susceptibility $\chi'(T)$ curves at frequencies 0.17 Hz, 1.7 Hz, 17 Hz, 170 Hz for $x = 0.3$ shows that the peak position of the $\chi'(T)$ curves is frequency dependent. It is noticed that the height of these peaks descends with increasing frequency which is a signature of spin glass (SG) like state. Figure 4(c) shows $M$ versus $T$ plots obtained from the field cooled warming
condition within the temperature range 10–300 K at 10,000 Oe (1 T) applied magnetic field. Sample with x = 0.1 shows a clear charge ordering at temperature $T_{co} = 225$ K and at the low temperature below $T_{co}$ the sample undergoes a second order phase transition from paramagnetic to ferromagnetic state. This transition is very broad suggesting a smearing of the transition due to lattice defects. In the sample with x = 0.3 a weak charge ordering at temperature $T_{co} = 211$ K is found and with decreasing temperature from $T_{co}$ the sample undergoes a second order phase transition from paramagnetic to ferromagnetic state. This transition is comparatively sharper than that of the sample with x = 0.1. This curve also shows a clear anti-ferromagnetic transition at $T = 25$ K for x = 0.3.

Because of smearing of the paramagnetic to the ferromagnetic transition the magnetocaloric effect is expected to be small and was not studied for x = 0.2. However, the magnetic entropy change ($-\Delta S_m$) for the sample with x = 0.1 and x = 0.3 shown in figure 4(d) was calculated from $M$ versus $T$ curves taken at $H = 10000$ Oe (1 T). For isothermal processes, total magnetic entropy change $\Delta S_m$ of a magnetic system due to application of a magnetic field $H$ is given by the Maxwell’s thermodynamic relation\cite{2}:

$$\Delta S_m = \int \left( \frac{\partial M}{\partial T} \right)_H dH$$

In order to evaluate this quantity we used an approximation of the above integral in the form

$$\Delta S_m = \int \left( \frac{\partial M}{\partial T} \right)_H \Delta H$$

The value of magnetic entropy change ($-\Delta S_m$) was 0.012 J K$^{-1}$ g$^{-1}$ K$^{-1}$ for x = 0.1 and 0.028 J K$^{-1}$ g$^{-1}$ K$^{-1}$ for x = 0.3 around $T = 66$ K for a magnetic field change $\Delta H = 10,000$ Oe (1 T).

Conclusion:

Polycrystalline samples of Sm$_{0.5}$Ca$_{0.5}$Sr$_x$MnO$_3$ were prepared by conventional solid-state reaction technique. All the compounds crystallize in single phase orthorhombic structure with space group Pnma. Present investigation shows that the structural and magnetic properties of Sm$_{0.5}$Ca$_{0.5}$Sr$_x$MnO$_3$ can be tuned by Sr doping. The substitution of Sr$^{2+}$ for Ca$^{2+}$ increases the lattice parameter, tolerance factor and the Curie temperature. Magnetic measurements show that all the samples exhibit a paramagnetic to ferromagnetic transition though a clear deviation from the mean-field Curie–Weiss behavior has been observed above $T_c$. The increase of tolerance factor and cell volume and decreasing of coercivity ($H_c$) due to the Sr doping for Ca plays an imperative role for A-site disorder which in turn shifted the Curie temperature from 22 K for x = 0.1 to 31 K for x = 0.3. It is also noted that the magnetization increases with increasing Sr content. Coercivity ($H_c$) decreases from 1238 Oe to 308 Oe with increasing Sr content and it is seen that the coercivity is temperature dependent.

In soft magnetic materials, the coercivity of perovskite usually depends on temperature. We suggest that the temperature dependence of the magento-crystalline anisotropy has a similar behavior. The sample with x = 0.1 shows a clear charge ordering at temperature $T_{co} = 225$ K and the charge ordering process is weakened lowering the $T_{co} = 211$ K for x = 0.3. The value of magnetic entropy change ($-\Delta S_m$) was 0.012 J K$^{-1}$ g$^{-1}$ K$^{-1}$ for x = 0.1 and 0.028 J K$^{-1}$ g$^{-1}$ K$^{-1}$ for x = 0.3 around $T = 66$ K for a magnetic field change $\Delta H = 10,000$ Oe (1 T). It is observed that the sample with x = 0.3 shows a spin-glass-like behavior at low temperature.

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References

[1] Anwar M S, Kumar S, Ahmed F, Kim G W and Koo B H 2012 J. Nanosci. Nanotechnol. 12 5523
[2] Bhatt R C, Singh S K, Srivastava P C, Agarwal S K and Awana A P S 2013 J. Alloy. Compd. 580 377
[3] Bahl C R H, Velázquez D, Nielsen K K, Engelbrecht K, Andersen K B, Bulatova R and Pryda N 2012 Appl. Phys. Lett. 100 12
[4] Phong P T, Khiem N V, Dai N V, Manh D H, Hong L V and Phuc N X 2009 J. Alloys Compd. 484 12
[5] Torrance J B, Lacorre P, Nazzal A I, Ansalado E J and Niedermayer C 1992 Phys. Rev. B 45 8209
[6] Rodriguez-Martinez L M and Attfield J P 1996 Cation disorder and size effects in magnetoresistive manganese oxide perovskites Phys. Rev. B 54 R15622–5
[7] Koubaa M, Cheikhrouhou-Koubaa W, Cheikhrouhoua A and Haghiri-Gosnet A-M 2008 Physica B 403 2477–83
[8] Kugel’ Kliment I et al 1982 The Jahn-Teller effect and magnetism: transition metal compounds Soviet Physics Uspekhi 25 231
[9] Tokura Y and Tomioka Y 1999 Colossal magnetoresistive manganites J. Magn. Magn. Mater. 200 1–23
[10] Ehsani M H, Kameli P, Ghazi M E, Razavi F S and Taheri M 2013 J. Appl. Phys. 114 223907
[11] Szymczak R, Czapela M, Kolano R, Kolano-Burian A, Krzymanska B and Szymczak H 2008 J. Mater. Sci. 43 1734–9
[12] Tomioka Y and Tokura Y 2004 Phys. Rev. B 70 014432
[13] Mleki A, Othmani S, Cheikhrouhou-Koubaa W, Kouba M and Cheikhrouhou A 2015 J. Alloy. Compd. accepted 645 559–65
[14] Tishin A M and Spichkin Y I 2003 The Magnetocaloric Effect and its Application (Bristol and Philadelphia: IOP publishing Ltd)