

Effect of doping concentration on micro strain in nanostructured Perovskite Manganites

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ABSTRACT - Microstrain in a crystal is the degree of distortion in the crystalline lattice. It is very important parameter of the material so far as the mechanical properties of the materials are concerned. The doped rare earth perovskite manganites of the general formula $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ various values of x are taken as $x=0.1, 0.2, 0.3, 0.4$ is synthesized using chemical rout method .The magnetic ion doped i.e Nickel doped Manganite are formed. Phase formation is confirmed using X-Ray diffraction. Crystallites size is calculated after calcination and after sintering. Crystallites size is formed between 15nm to 40nm. Williamson hall formula is used to calculate micro-strain in the samples for all four concentrations. The effect on micro-strain for various concentrations before sintering and after sintering is studied .It is observed that micro-strain depends upon doping concentration .Also there is effect of sintering on micro-strain. In further study different ions like Co, Cr, Fe can be taken and effect on micro-strain can be observed.

Keywords—Crystalline Size; Williamsons Hall; Sol Gel; Microstrain; Perovskite;

1. INTRODUCTION

Perovskite manganites with the chemical composition $\text{RE}_{1-x}\text{A}_x\text{MnO}_3$ (where RE = trivalent rare-earth ions and A = divalent alkaline-earth ions) constitute an important class of strongly correlated oxide materials owing to their exceptional magnetic, electrical and structural properties. Since the discovery of colossal magnetoresistance (CMR), these compounds have attracted widespread attention for both fundamental studies and technological applications [1–3]. The substitution of trivalent rare-earth ions with divalent cations generates mixed $\text{Mn}^{3+}/\text{Mn}^{4+}$ valence states, thereby facilitating the double-exchange interaction responsible for ferromagnetism and enhanced electrical conductivity [4]. Furthermore, electron–phonon interactions arising from lattice polarons and Jahn–Teller distortions contribute significantly to their complex physical behaviour. The coexistence and competition among these interactions give rise to a variety of electronic and magnetic phases, making manganites an active area of research. The earliest evidence of ferromagnetism in mixed-valence manganites was reported by Jonker and Van Santen in 1950 for $(\text{La,Ca})\text{MnO}_3$ and $(\text{La,Sr})\text{MnO}_3$, marking the beginning of extensive investigations into these multifunctional

perovskite oxides [5]. The parent compound, LaMnO_3 , is recognized as a layered antiferromagnetic (AFM) charge-transfer insulator [1–4]. Its magnetic and electrical properties are primarily governed by the mixed valence states of manganese, namely Mn^{3+} and Mn^{4+} , with electronic configurations of $t_{2g}e_g$ and $t_{2g}e_{0g}$, respectively. The double-exchange interaction between these ions plays a crucial role in determining the magnetic ordering and electrical conductivity of the material [5]. The three t_{2g} electrons constitute a localized core spin of ($S = 3/2$), while the additional e_g electron associated with the Mn^{3+} ion occupies a higher-energy orbital, contributing to the layered antiferromagnetic behaviour through orbital interactions [5–11].

ABO_3 are manganite (Rare earth manganites) has a perovskite structure as shown in the Figure 1. In the last few years for A and B various rare earths (or alkaline earths) and transition metal ions materials are attempted with different percentage and various physical properties like magnetization, transport properties are studied of these compounds. These material shows useful properties which can have potential applications. Manganites were first synthesized in 1950 by Jonkar and Santen. Microstrain of a

crystal is an important parameter as magnetic properties of the materials are concerned. Crystal micro-strain is due substitutional doping. This doping changes the bond length as well as bond angle. Due to the doping of the transition metals of different ion sizes in the crystal macrostrain is developed in the crystal and can be calculated. Negative micro-strain is also expected for the ions having higher ion size like Cr^{3+} , Co^{3+} [12-15].

To study the microstructural properties of Manganites (ABO_3), It is synthesized by taking compositions of A as given below i.e. by taking $\text{A1}=\text{La}_{1-x}$ and $\text{A2}=\text{Sr}_x$, $\text{A}=\text{A1}+\text{A2}$, and $x = 0.3$ and by taking different compositions of B as given below i.e. $\text{B}=\text{B1}+\text{B2}$, $\text{B1}=\text{Mn}_{1-x}$, $\text{B2}=(\text{Ni})_x$ at different values of x like 0.1, 0.2, 0.3, 0.4 [16, 17]. This synthesis will be by sol gel chemical route process. The ratio of $\text{Mn}^{3+}/\text{Mn}^{4+}$ depends on B-site doping also. The magnetic ions introduced by B-site doping increase the complexity of the magnetic exchange interactions between B-site ions by creating additional exchange pathways and competing interactions. B-site can be doped with transition metals (Ni, V, Fe, Co, Cr, and Cu) [1]. This leads to change the micro strain and subsequently changes T_c . When B site is doped with Ni for $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_3$, the T_c decreased significantly with the doping content and goes below the room temperature. The increasing trend of T_c is observed when the B site was doped with V. The $\text{La}_{0.67}\text{Pb}_{0.33}\text{Mn}_{1-x}\text{Co}_x\text{O}_3$ ($0.15 \leq x \leq 0.3$) material studied by N. Dhahri [10, 11], it is observed that T_c drops drastically when Co contents increases.

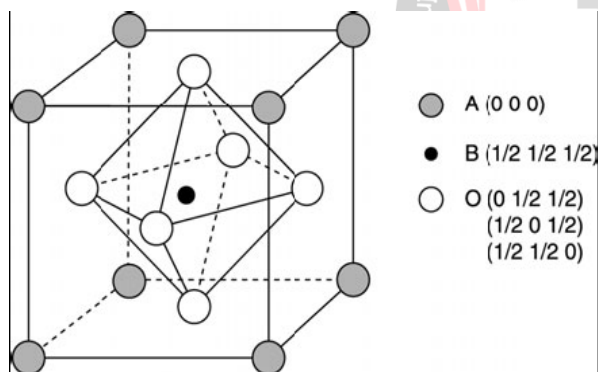


Figure 1: Perovskite Structure

2. EXPERIMENTAL DETAILS

2.1. Synthesis

The manganite nanoparticle of different compositions can be synthesized by standard sol-gel technique which has potential advantages over other methods. Here Sol-gel routes method is used because it produces a very high quality, homogeneous and fine nanoparticle samples. This is the most appropriate method to produce high-quality Magnetic Oxide Nanoparticles (MONPs) in comparison to other physical and chemical methods. Sol-gel synthesis is one of the simple, fastest and most economical, and has also its own advantages like low

processing temperature, homogeneity of the produced material.

2.2. Materials

In this synthesis following materials can be taken as a basic or raw materials:

- Lanthanum Oxide for La
- Strontium Nitrate for Sr
- Manganese Nitrate or Manganese Acetate depending on availability

For above mentioned material chlorides also can be used but it may affects the purity of the synthesized material. It is very difficult to remove the impurity of chlorines. For Ni nitrate should be used.

2.3. Chemical Process

The various steps which are to be carried out in this method is given below with the help of flow chart

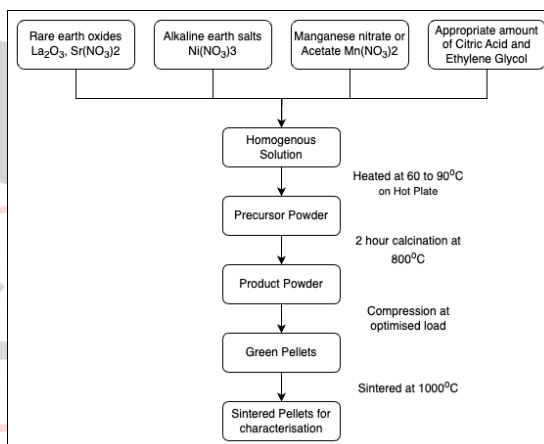


Figure 2: Methodology

3. Results and Discussion

X-Ray Diffraction (XRD) of these samples after calcination i.e. before sintering is shown in Figure 3, Figure 4, Figure 5 and Figure 6 and after sintering is shown in Figure 7, Figure 8, Figure 9 and Figure 10. This confirms the phase formation.

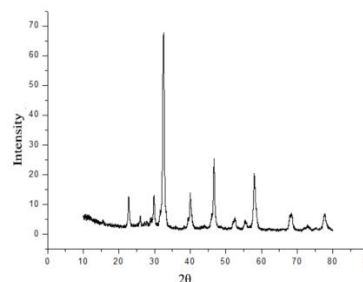


Figure 3: $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$ before Sintering

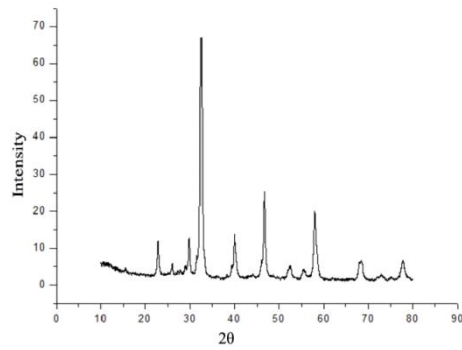


Figure 4: $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$ before Sintering

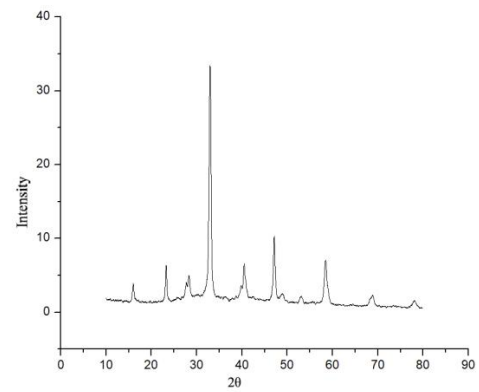


Figure 8: $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$ after Sintering

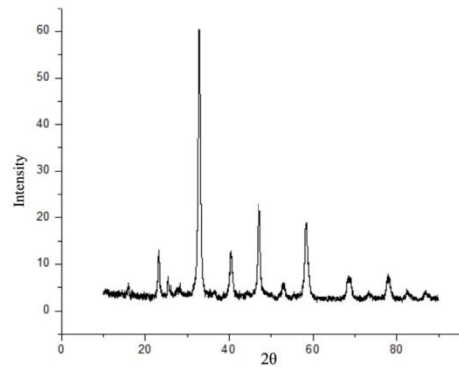


Figure 5: $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.7}\text{Ni}_{0.3}\text{O}_3$ before Sintering

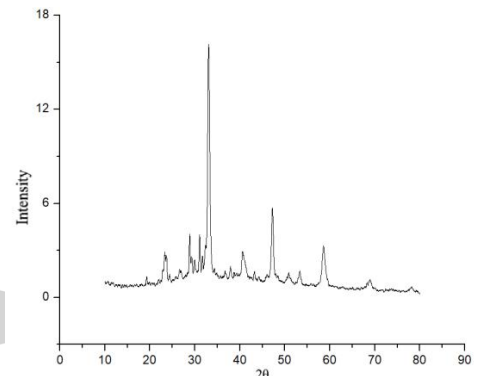


Figure 9: $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.7}\text{Ni}_{0.3}\text{O}_3$ after Sintering

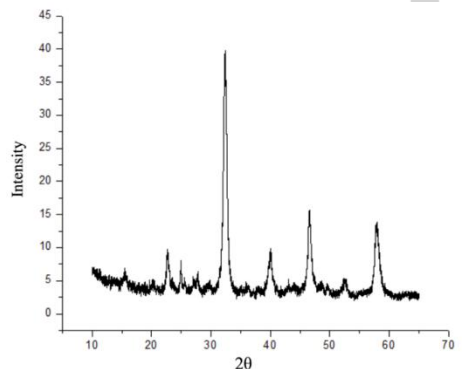


Figure 6: $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.6}\text{Ni}_{0.4}\text{O}_3$ before Sintering

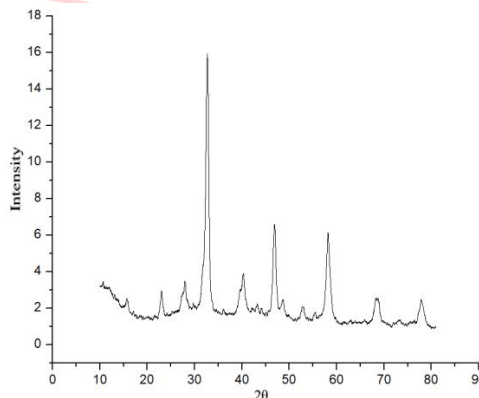


Figure 10: $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.6}\text{Ni}_{0.4}\text{O}_3$ after Sintering

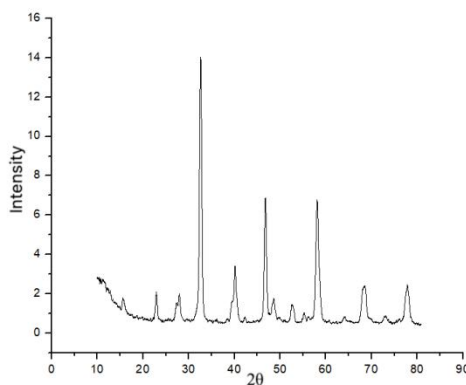


Figure 7: $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$ after Sintering

From the characteristics angles ' θ ' for the first three peaks are found and β i.e. full width half maxima is also calculated from Figure 2 to 10 and the values are reported in the Table from 1 to 8.

According to Williamson and Hall method, when a product of full width at the half maxima of the peak of the X-Ray diffraction and $\cos\theta$ on y axis against $\sin\theta$ on x axis is plotted, from the slope of the plot we get the strain component and the particle size component from the y intercept [3].

Table 1: $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$ before Sintering

	2 θ	θ	$\sin \theta$	$\cos \theta$	FWHM, β (Rad)	4 $\sin \theta$	$\beta \cos \theta$
Peak 1	32.40 16	16.20 08	0.27 91	0.96 02	0.01133067 8	1.1164552 11	0.0108803 74
Peak 2	46.59 47	23.29 73	0.39 56	0.91 84	0.00947713 8	1.5826133 43	0.0087038 03
Peak 3	57.92 33	28.96 16	0.48 44	0.87 48	0.01626297 8	1.9376084 8	0.0142275 93

Table 2: $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$ before Sintering

	2 θ	θ	$\sin \theta$	$\cos \theta$	FWHM, β (Rad)	4 $\sin \theta$	$\beta \cos \theta$
Peak 1	36.62 28	16.31 14	0.28 09	0.95 97	0.01125213 8	1.1238705 84	0.0107988 71
Peak 2	46.87 11	23.43 55	0.39 78	0.91 74	0.01085594 8	1.5914731 82	0.0099597 08
Peak 3	58.19 94	29.09 97	0.48 65	0.87 36	0.01630137 5	1.9460376 62	0.0142421 09

Table 3: $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.7}\text{Ni}_{0.3}\text{O}_3$ before Sintering

	2 θ	θ	$\sin \theta$	$\cos \theta$	FWHM, β (Rad)	4 $\sin \theta$	$\beta \cos \theta$
Peak 1	32.8 369	16.41 845	0.282 761	0.959 19	0.011370 82	1.13104 395	0.01090 6781
Peak 2	47.1 516	23.57 58	0.400 114	0.916 465	0.011178 834	1.60045 4969	0.01024 5015
Peak 3	58.4 618	29.23 09	0.488 51	0.872 559	0.016427 039	1.95403 8188	0.01433 3553

Table 4: $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.6}\text{Ni}_{0.4}\text{O}_3$ before Sintering

	2 θ	θ	$\sin \theta$	$\cos \theta$	FWHM, β (Rad)	4 $\sin \theta$	$\beta \cos \theta$
Peak 1	32.44 76	16.223 8	0.2794 99	0.9601 46	0.0117408 3	1.117997 63	0.011272 909
Peak 2	46.54 41	23.272 05	0.3952 48	0.9185 75	0.0147218 52	1.580990 391	0.013523 12
Peak 3	57.95 49	28.977 45	0.4846 43	0.8747 12	0.0167045 46	1.938573 711	0.014611 664

Table 5: $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$ after Sintering

	2 θ	θ	$\sin \theta$	$\cos \theta$	FWHM, β (Rad)	4 $\sin \theta$	$\beta \cos \theta$
Peak 1	32.6 16.3	16.3 77	0.2807 77	0.9597 73	0.01029744 3	1.1231064 44	0.0098832 09
Peak 2	46.7 6	23.3 8	0.3969 78	0.9178 28	0.01064650 8	1.5879130 48	0.0097716 64
Peak 3	58.1 5	29.0 51	0.4857 97	0.8740 97	0.01466076 6	1.9430043 05	0.0128149 34

Table 6: $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$ after Sintering

	2 θ	θ	$\sin \theta$	$\cos \theta$	FWHM, β (Rad)	4 $\sin \theta$	$\beta \cos \theta$
Peak 1	32.9 7	16.4 85	0.2838 75	0.9588 61	0.01012291 61	1.135501 442	0.009706 465
Peak 2	47.1 2	23.5 6	0.3998 61	0.9165 76	0.00942477 8	1.599443 596	0.008638 524
Peak 3	58.4 4	29.2 2	0.4883 43	0.8726 52	0.01518436 4	1.953373 9	0.013250 659

Table 7: $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.7}\text{Ni}_{0.3}\text{O}_3$ after Sintering

	2 θ	θ	$\sin \theta$	$\cos \theta$	FWHM, β (Rad)	4 $\sin \theta$	$\beta \cos \theta$
Peak 1	33.4 16.7	16.7 73	0.2874 73	0.9577 89	0.01047197 6	1.149891 545	0.010029 941
Peak 2	47.2 3	23.6 15	0.4007 41	0.9161 91	0.01029744 3	1.602963 673	0.009434 429
Peak 3	58.6 29.3	29.3 62	0.4895 62	0.8719 69	0.01727876 69	1.958247 76	0.015066 535

Table 8: $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.6}\text{Ni}_{0.4}\text{O}_3$ after Sintering

	2 θ	θ	$\sin \theta$	$\cos \theta$	FWHM, β (Rad)	4 $\sin \theta$	$\beta \cos \theta$
Peak 1	32.6 4	16.3 2	0.2811 12	0.9596 75	0.01378810 1	1.1244470 11	0.0132320 96
Peak 2	46.9 2	23.4 6	0.3982 6	0.9172 73	0.01623156 2	1.5930396 79	0.0148887 67
Peak 3	58.1 4	29.0 7	0.4860 56	0.8739 28	0.02984513 28	1.9442251 48	0.0260824 8

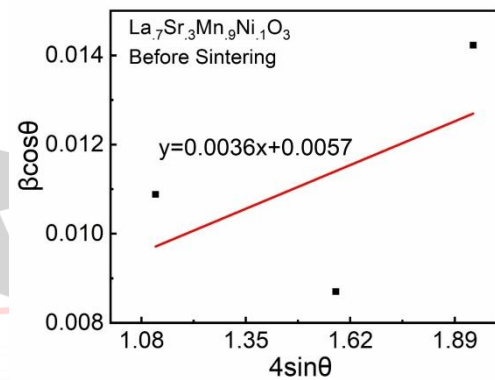


Figure 11: W-H plot for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$ before Sintering (Parameters reported in Table 1)

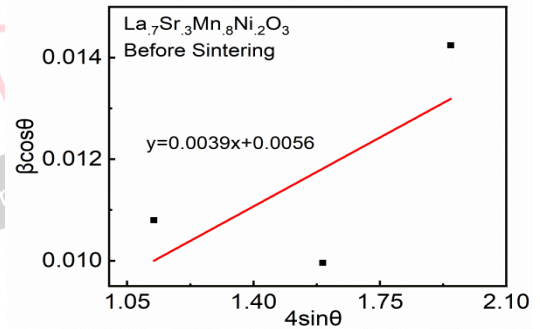


Figure 12: W-H plot for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$ before Sintering (Parameters reported in Table 2)

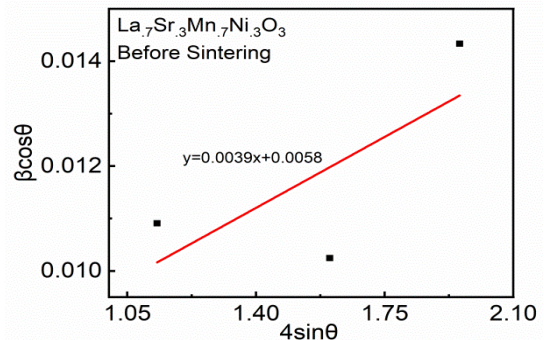


Figure 13: W-H $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.7}\text{Ni}_{0.3}\text{O}_3$ before Sintering (Parameters reported in Table 3)

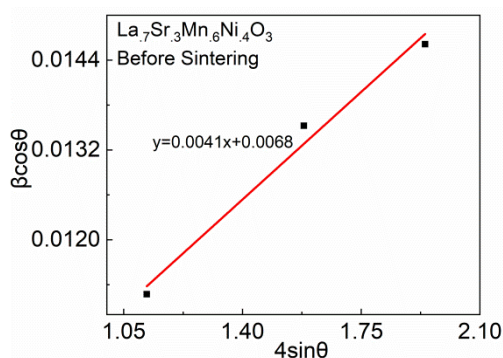


Figure 14: W-H plot for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.6}\text{Ni}_{0.4}\text{O}_3$ before Sintering (Parameters reported in Table 4)

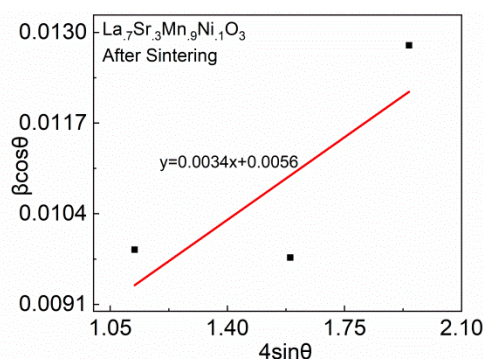


Figure 15: W-H plot for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.5}\text{Ni}_{0.5}\text{O}_3$ (Parameters reported in Table 5)

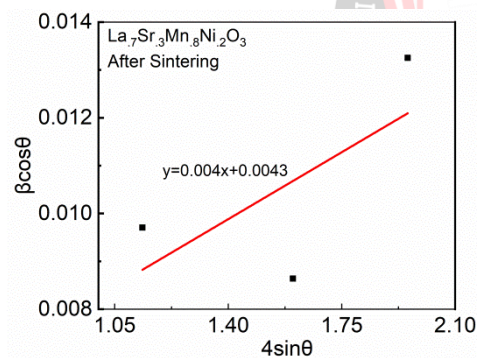


Figure 16: W-H plot for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.4}\text{Ni}_{0.6}\text{O}_3$ after Sintering (Parameters reported in Table 6)

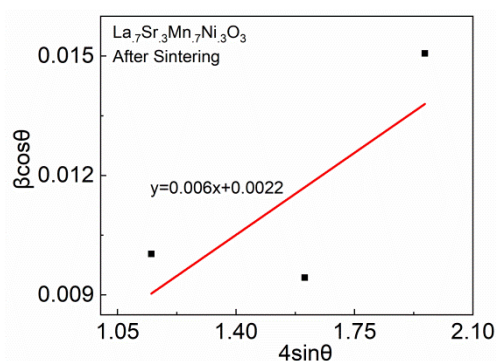


Figure 17: WH plot for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.3}\text{Ni}_{0.7}\text{O}_3$ after Sintering (Parameters reported in Table 7)

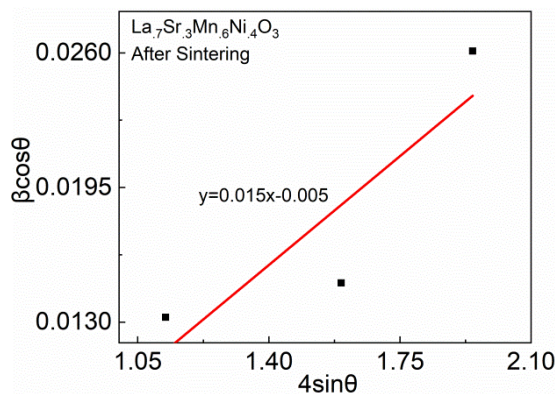


Figure 18: W-H plot for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.6}\text{Ni}_{0.4}\text{O}_3$ after Sintering (Parameters reported in Table 8)

The micro strains and grain sizes of the crystallites before sintering are determined from Figure 11 to 14. The percentage of Ni is varied to 10 %, 20%, 30% and 40% and is mentioned in Table 9. The micro strains and grain sizes of the crystallites after sintering are determined from Figure 15 to 18. The percentage of Ni is varied to 10%, 20%, 30% and 40% and is mentioned in Table 10. It has been observed that micro strain increases with the increasing percentage of Ni in both the case i.e. before sintering and after sintering .Crystallite size is also increased due to sintering .

Table 9: Before sintering

Sr. No	Percentage of Ni	Microstrain	Crystallite Size
1	10	00.36	54.035
2	20	00.39	55
3	30	00.39	53.103
4	40	00.41	45.294

Table 10: After sintering

Sr. No	Percentage of Ni	Microstrain	Crystallite Size
1	10	00.34	55
2	20	00.4	66.956
3	30	00.59	133.913
4	40	1.5	58.113

Conclusion

The present study demonstrates that the micro-strain in Ni-doped rare-earth perovskite manganites, $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ ($x = 0.1, 0.2, 0.3$, and 0.4), is strongly influenced by both the Ni doping concentration and the sintering process. X-ray diffraction analysis confirmed the successful formation of the single-phase perovskite structure, while the crystallite size was found to lie in the nanometre range (15–40 nm) after calcination and sintering. The Williamson–Hall method effectively quantified the lattice micro-strain, revealing systematic variations with increasing Ni content, indicating that substitution of Mn by Ni introduces lattice distortion due to differences in ionic radii and local structural disorder. Furthermore, sintering significantly modified the micro-strain, suggesting improved crystallinity and relaxation of internal lattice defects. These findings highlight the importance of controlling dopant concentration and thermal treatment to

tailor the structural properties of manganite materials, which directly influence their mechanical and functional characteristics. Future investigations involving other transition-metal dopants such as Co, Cr, and Fe may provide further insights into the relationship between dopant-induced lattice distortion and the resulting physical properties of perovskite manganites.

Future Aspects

Further study is possible by doping different magnetic ions. The micro-strain in the crystal due to doping it increases carrier localization, decreases long-range ferromagnetic ordering, and promotes magnetic phase separation and cluster-glass behaviour. Consequently, increasing micro-strain in general decrease the Curie temperature and saturation magnetization, along with enhanced magnetic irreversibility. These properties can be used for some potential applications like Magnetic sensors, Spintronic devices, Magnetic field sensors, Magnetic memory devices.

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