

# Local electronic structure of heavy-ion irradiated nano-crystalline stoichiometric $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ particles using high-resolution Mössbauer spectroscopy

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## ABSTRACT

Nanocrystalline stoichiometric  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$  manganites synthesized by sol gel technique were irradiated by 200 MeV  $\text{Ag}^{+16}$  ion beam at various fluences and investigated by X-ray diffraction (XRD), magnetization and high resolution Mössbauer spectroscopic techniques. The analysis of Mössbauer patterns were done using Kopcewicz et al. (2004) proposition considering Double exchange mechanism. Both XRD and Mössbauer spectroscopic analysis indicated isostructural vacancy formation at Mn site at the fluence  $5 \times 10^{12}$  ions/cm<sup>2</sup>. The system showed amorphous phase at the higher fluence of  $1 \times 10^{13}$  ions/cm<sup>2</sup>. The local electronic environments seen through high resolution Mössbauer spectroscopic technique on the irradiated systems were understood in terms of ferromagnetic coupling between different Mn environment surrounding Fe ions. This proposition is supported by enhanced magnetization observed in the irradiated samples (Kopcewicz et al., 2004). The similarity to the hydrostatic applied pressure (at low value) is seen through the transformation from  $\text{Fe}^{4+}$  to  $\text{Fe}^{3+}$  at low fluence. Copyright © 2013 VBRI press.

**Keywords:** Mössbauer spectroscopy; swift heavy ions irradiation; X-ray diffraction; ferromagnetic coupling; Magnetization; nanocrystalline; vacancy-doped manganites; perovskites.



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## Introduction

Modification in the physical properties of solids under the influences of irradiation with energetic particles such as creation of defects states, phase changes, amorphization etc are well known defect [1, 2]. The irradiation-induced degradation of metals have been observed in fusion reactors despite the observed damages, irradiation also have shown beneficial effects on materials especially in semiconductor industry through ion-implantation and in biophysics

through radiation assisted treatment of cancer. Ion beam irradiation has been found to be an important way to induce non-equilibrium states in matter [3]. Defects, disorders and local structure modification by ion-beam irradiation can be useful in tailoring modification the Colossal Magneto-Resistive (CMR) manganites material. Since electrical and magnetic properties are closely linked with the electronic bonding of  $Mn^{3+}$ -O- $Mn^{4+}$  network, any modification in local structure induced by energetic ion beam is expected to affect bond angle and bond length between Mn and O [4,5]. It has been reported that one vacancy is produced per hundreds of unit cells in a manganites system by ion irradiation appreciable changes in the material properties [6].

The effect of SHI irradiation, creating columnar defects along the trajectories of ions in the bulk materials have been well explained through coulomb explosion and thermal spike models [7, 8]. However, the production of defects in irradiated nano -systems is different from that in bulk materials [9] giving rise to quite unexpected results, probably due to effects of ion beam heating and vanishingly small probability of defect production in a very thin target. A microscopic understanding therefore, is required of defect production in nano system under irradiation to improvise the properties of nano materials. The nanocrystalline system is characterized through its high surface area and high surface to volume ratio, while the ion beam interaction in the high surface area results into large sputtering yield, the high surface to volume ratio gives rise to enhanced annealing. In contrast to bulk system where all the energy is dispersed in the total area of the sample, only a small part of projected energy is deposited in nano-materials reducing the cross-section of defect production. Correspondingly the amount of total damage in nano materials decreases with the particle energy, contrary to the situation in bulk objects.

La based manganites,  $Ln_{1-x}A_xMnO_3$  (Ln- a trivalent Lanthanide cation; A-a divalent earth cation Ca,Ba,Sr) exhibits varieties of interesting magnetic and electrical properties which can be tuned by the nature and stoichiometry of Ln and A. Doping with divalent cation transforms  $Mn^{3+}$  to  $Mn^{4+}$  ions and with sufficient doping, the holes become mobile transforming an insulator to metallic nature. Conventionally, double exchange mechanism has been invoked to explain the dramatic increase in conductivity through alignment of spins parallel and resulting into simultaneous metallic ferromagnetic ordering. In the doping range of  $x \sim 0.2-0.5$ ,  $La_{1-x}Sr_xMnO_3$  behaves as ferromagnetic metal at low temperature and a poorly conducting paramagnet at high temperature [10]. Nanoparticles of  $La_{0.8}Sr_{0.2}MnO_3$  showed enhanced Curie temperature (323°K) markedly higher than corresponding bulk single crystalline sample (302°K) [11, 12, 13]. Similar variation in Curie temperature  $T_c$  is achieved under hydrostatic pressure or with irradiation without changing doping concentration [14, 2]. Swift heavy ion (SHI) irradiation develops a permanent strain in the lattice while hydrostatic pressure affects temporarily. Experimental studies have been carried out on bulk  $La_{2-x}Ca_xMnO_3$ ,  $Pr_{2-x}Ca_xMnO_3$  and  $Nd_{2-x}Ca_xMnO_3$  manganites under applied hydrostatic pressure and under irradiation using various techniques but very little work has been done on SHI

irradiated nanocrystalline  $(La,Sr)_2(Mn,Fe)O$  systems especially using Mössbauer spectroscopic techniques. This technique has gained tremendous popularity after its inclusion in Mars Expeditions [15].

Detailed studies on nanocrystalline stoichiometric sample  $La_{0.8}Sr_{0.2}Mn_{0.8}Fe_{0.2}O_3$  has been done under high pressure using electrical resistivity, Laser Raman and Mössbauer spectroscopy. The substitution of transition metal (like Fe) leads to the formation of  $Fe^{4+}$  in the solid phase leading to important modifications in the various properties of  $(La,Sr)(Mn,Fe)O_3$  systems. A sudden increase in isomer shift in Mössbauer measurements on nanocrystalline sample showed first order phase transition at 0.52 GPa indicated by the transformation of  $Fe^{4+}$  (in cubic symmetry) into the high spin  $Fe^{3+}$ (in octahedral symmetry). Another transition at 3.6 GPa represented by  $Fe^{3+}$  in a single environment indicated complete transformation of ambient orthorhombic phase into monoclinic phase. The first order transition was explained as cross over from localized electron to band magnetism through crystal field effect which splits 3d states of Fe into  $t_{2g}$  and  $e_g$  orbitals. A cooperative Jahn-Teller distortion and the external pressure together drives the antiferromagnetically coupled  $e_g$  to align along (001) planes giving rise to ferromagnetic ordering. Laser Raman spectroscopy also supported the conclusion at 0.52 GPa by complete vanishing of the mode representing Fe and by phonon softening of the mode indicating structural instabilities in  $MnO_4$  octahedra [16-19].

$^{57}Fe$  Mössbauer spectroscopy is an effective experimental tool to extract information about local electronic structure, symmetry and magnetic ordering surrounding Fe nucleus through its parameters: Isomer shift (IS), Quadrupole splitting (QS) and magnetic hyperfine field (HF). This technique also allows one to determine the valence of the Fe ions, site populations and variations in chemical environment around Fe nucleus.

Present report focuses the variation in crystal and electronic structures in nanocrystalline stoichiometric perovskite manganite  $La_{0.8}Sr_{0.2}Mn_{0.8}Fe_{0.2}O_3$  under the effect of SHI irradiation by 200MeV  $Ag^{+16}$  ions using X-ray diffraction and high-resolution Mössbauer spectroscopic techniques. X-ray diffraction and Magnetic measurements are macroscopic probes associating all the atoms to participate while  $^{57}Fe$  Mössbauer spectroscopic measurements, a local probe, negotiates with lattice structure and its variations microscopically through indirect study on Fe ions present in the system. The advantage of this method is the sensitivity of the Mossbauer parameters to external effects such as hydrostatic pressure, temperature and irradiation etc. Such details, has not been reported till, would be useful in understanding the mechanism under study by irradiation.

## Experimental

### Materials

High purity (>99.95%) lanthanum carbonate, strontium carbonate, Fe and Mn metal from Sigma Aldrich, U.K. were used for the synthesis of the nanocrystalline sample. Anhydrous Lanthanum carbonate was used for synthesis by heating to the powder 1000°C for 4 hours. Enriched iron

procured from Cyclotron, Germany was used for making Mössbauer absorbers.

### Method

High Purity and homogeneous nano-crystalline powder  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$  (LSMO) sample was synthesized using sol gel technique [16]. To obtain appropriate amount of Mössbauer ions, 2% of enriched Fe atoms were included during sample preparation. Stoichiometric amount of  $\text{La}_2\text{CO}_3$ ,  $\text{SrCO}_3$ , Mn and Fe were dissolved in nitric acid and double distilled water and pH was controlled. The solution was mixed with 1 gram of urea and heated to dehydrate and form a gel. The gel was dried and annealed at  $600^\circ\text{C}$  for 12 hours. Sample was characterized by taking x-ray diffraction (XRD) patterns using  $\text{FeK}\alpha$  /  $\text{CuK}\alpha$  radiations. The measurements were carried out above  $30^\circ$  using  $\text{Cu K}\alpha$  radiation due to some technical restrictions. The Debye - Scherrer equation applied on the broadened x-ray peaks determined the particle size to be  $\sim 140\text{\AA}$  [20]. Oxygen stoichiometry was evaluated using well known iodometric titration performed using KI, Sodium thio-sulphate solution with starch as an indicator.

For implantation free radiation damage, thickness of the absorber is an important and crucial parameter. Estimated thickness of the samples through SRIM was  $70\mu\text{m}$ . To achieve such thin absorber, finely powdered sample was brushed uniformly over thin pure aluminum foil ( $1\text{cm} \times 1\text{cm}$ ) coated with very thin layer of adhesive and extra powder adhered was dusted off. Care was taken to prepare samples of identical thicknesses. These thin absorber were mounted on an electrically insulated sample ladder placed in a secondary electron suppressed geometry and irradiated at room temperature with  $200\text{MeV Ag}^{+16}$  ion beam using  $15\text{MV}$  Tandem accelerator with fluence  $1 \times 10^{11}$ ,  $5 \times 10^{11}$ ,  $1 \times 10^{12}$ ,  $5 \times 10^{12}$  and  $1 \times 10^{13}$  ions/ $\text{cm}^2$  with low beam current  $0.5\text{pA}$  ( $\text{pA} = \text{current in nA} \times \text{charge of the particle}$ ) to avoid heating effects. Uniform exposure in the sample was maintained using magnetic scanner, the fluence was measured by collecting charge falling on the sample through scalar counter and ladder current was integrated with a digital current integrator.

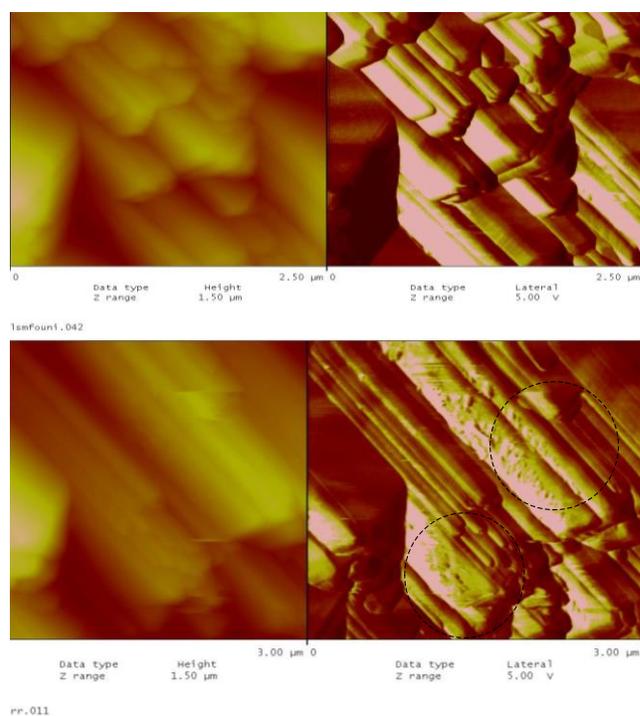
Experimental Mössbauer set up consists of  $10\text{mCi } ^{57}\text{Co}(\text{Rh})$  point source (active area  $0.5 \times 0.5 \text{ mm}^2$ ) at constant acceleration mode, Si-PIN solid state XR-100CR (amptek make) detector and CMCA-550 data acquisition module (Wissel make) for data collection. Mössbauer measurements were carried out by providing Doppler shift to the source. To achieve the 'high resolution Mössbauer measurements' under laboratory conditions, we adopted the Doppler shift corresponding to inner two lines of the natural Fe spectrum (between velocity range of  $\sim -2 \text{ mm/sec}$  to  $+2 \text{ mm/sec}$ ) which increased the sensitivity per channel of the spectrum. Mössbauer parameters- Isomer shift (IS), Quadrupole splittings (QS) and site population were determined by using usual analysis programme of Jernberg and Sundquist [21] with an appreciable goodness of fit parameter. Magnetization measurements were carried out using PARC make Vibrating Sample Magnetometer and close cycle refrigerator cryostat with temperature controller RMC model LTS-22J. Walker Scientific Co. HS-1050 electromagnet was employed for DC magnetic field up to

$9.5 \text{ KG}$  and field was measured using Lake Shore Cryotronic Gauss meter (Model 420) and a Hall Probe.

AFM measurements were carried out using Nanoscope-E of Digital Instruments, USA.  $\text{Si}_3\text{N}_4$  cantilevers of  $\sim 100\mu\text{m}$  length with a spring constant of  $0.58\text{N/m}$  have been employed in contact mode. Measurements were carried out on the sample prepared by spraying the powdered specimen and fixing it on a glass slide using acetone.

### Results and discussion

The Sol-gel technique is well established for the synthesis of homogenous, single phase, nano crystalline perovskite manganites and the heat-treatment temperature decides the particle size. Fig. 1 shows the AFM and LFM images of images of the unirradiated stoichiometric  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$  and irradiated sample to  $5 \times 10^{12}$  ions/ $\text{cm}^2$  fluence.



**Fig. 1.** LFM of stoichiometric  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$  sample before (top) and after (bottom) irradiation. The dotted circle (bottom) shows the pits formed due to irradiation.

A clear visible difference in the morphology of the surface layers of the sample due to the impinging ions is observed. Smoothness in the unirradiated sample contrasted by pits (marked in circle) in the irradiated sample. Morphological nonuniformity after irradiation indicates expected localization of defects for nanocrystalline materials as compared to the bulk where the energy is distributed all over the area of the specimen. Enhancement of local temperature prompting rapid ejection of matter due to swift heavy ion tracks may be the reason for formation of pits. Such exotic nanoparticle sputtering is seen in interstellar dust grains by cosmic ray ions [22, 23] and the total amount of damage to a nanoscale object decreases with the particle energy.

**Fig. 2** shows the XRD patterns of both pristine and irradiated stoichiometric compounds spread on Al foils using FeK $\alpha$  as x-radiation. All the prominent peaks are indexed for orthorhombic structure. The lattice parameters with various fluences are listed in **Table 1**.

The effect of irradiation could be realized as repopulation of the planes. Irradiated system at fluence of  $1 \times 10^{11}$  ions/cm $^2$  show prominent enhancement in (111) plane indicating relocations of the atom without changing the structure. The lattice parameters 'a' and 'c' remains almost the same but decrease in the value of 'b', decreasing consequences into reduction in the volume. Further increase in the fluence to  $5 \times 10^{12}$  ion/cm $^2$  showed prominent increase in the intensity of peaks around  $20^\circ$  indexed as (001) and (010) planes. Such an enhancement in these peaks might suggest the vacancy creation at the Mn-site [24]. Thus one could infer that the effect of the irradiation is to redistribute the atoms and to create vacancies at the various lattices. To understand the effect of vacancy in the La-or Mn-sites, the samples were synthesized with vacancies at La and Mn sites and structural variations were studied using XRD. **Fig. 2(A)** and **Table 1** compares XRD patterns and lattice parameters of the nanocrystalline stoichiometric sample  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$  with nanocrystalline vacancy-doped  $\text{La}_{0.9}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_{3.15}$  (named as La-deficient) and  $\text{La}_{0.86}\text{Sr}_{0.14}\text{Mn}_{0.80}\text{Fe}_{0.16}\text{O}_{2.91}$  (named as Mn-deficient) samples.

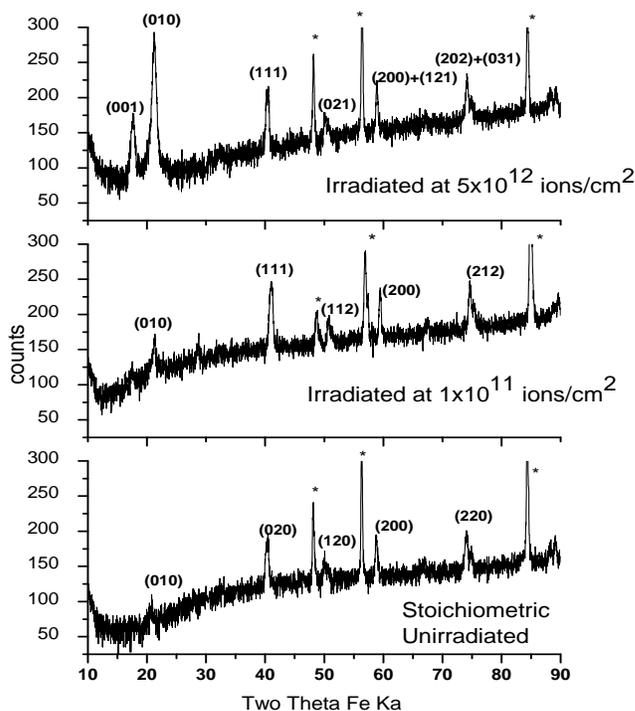
**Table 1:** Lattice parameters of various samples investigated in this study.

Sample	a (Å)	b (Å)	c (Å)	v (Å $^3$ )
Pristine-stoichiometric	3.91	5.56	6.32	137.39
$1 \times 10^{11}$ ions/cm $^2$	3.92	5.20	6.32	128.83
$5 \times 10^{12}$ ions/cm $^2$	3.83	6.97	5.98	113.83
La-deficient	3.85	5.12	5.99	118.07
Mn-deficient	3.81	5.12	6.13	119.58

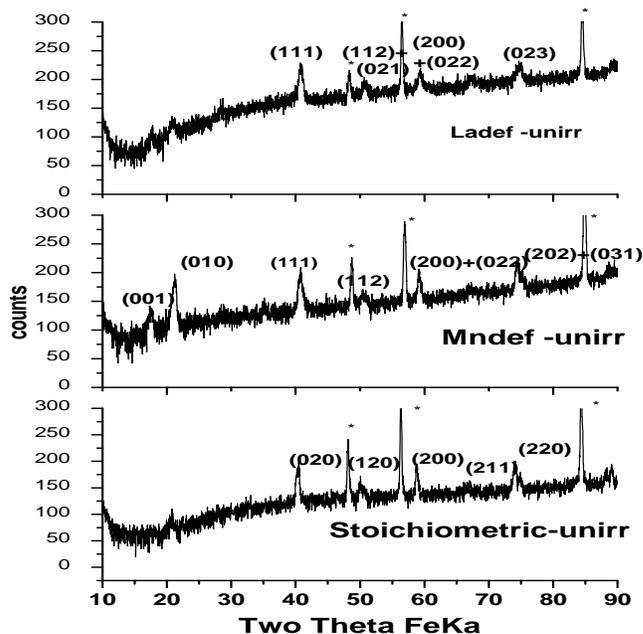
The prominent peaks indexed as (001) and (010) in Mn-deficient sample justifies our proposition. Detailed study of peak (111) with reference to Al peak (used as calibrant) would be interesting to study to understand the effect of irradiation on the stoichiometric sample. Still further increase in fluence with  $1 \times 10^{13}$  ions/cm $^2$ , broadening in all the XRD peaks were observed inferring the amorphous nature of the system (**Fig. 2B**). The unchanged peak positions referred to the structural stability of the lattice. The local temperature increment and sudden quenching might be the reason for randomization of crystallites.

$^{57}\text{Fe}$  Mössbauer spectroscopy is a sensitive technique which could identify the different lattice conditions of Fe ion in a lattice through the Mössbauer parameters. Isomer shift (IS) is proportional to s-electron density at the Fe nucleus primarily influenced by the valence of the Fe cation and the octahedral volume. Quadrupole splitting (QS) is related strongly to the non-cubic distortion in the iron containing octahedral site. There are two contributions towards QS-first the valence term that comes from the spatial extension of the valence electron clouds and the second is the lattice term influenced by nearby ions in the crystal lattice. **Fig. 3** shows Mössbauer spectra of both pristine and irradiated stoichiometric  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$

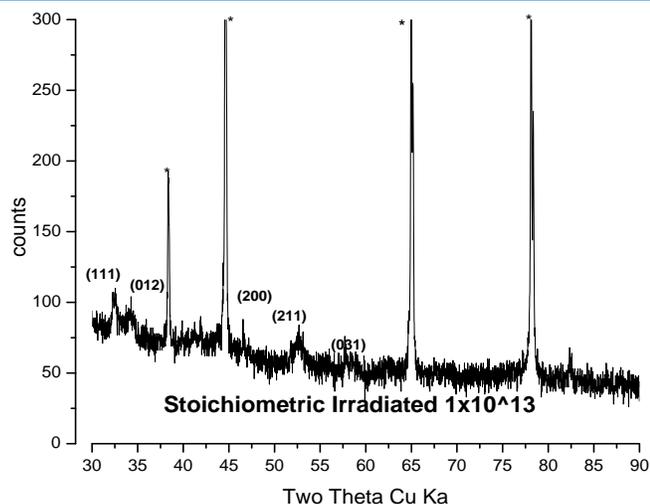
compounds. **Table 2** summarizes the analyzed Mössbauer parameters of the pristine and irradiated stoichiometric compounds at various fluences  $1 \times 10^{11}$ ,  $1 \times 10^{12}$ ,  $5 \times 10^{12}$  and  $1 \times 10^{13}$  ions/cm $^2$ .



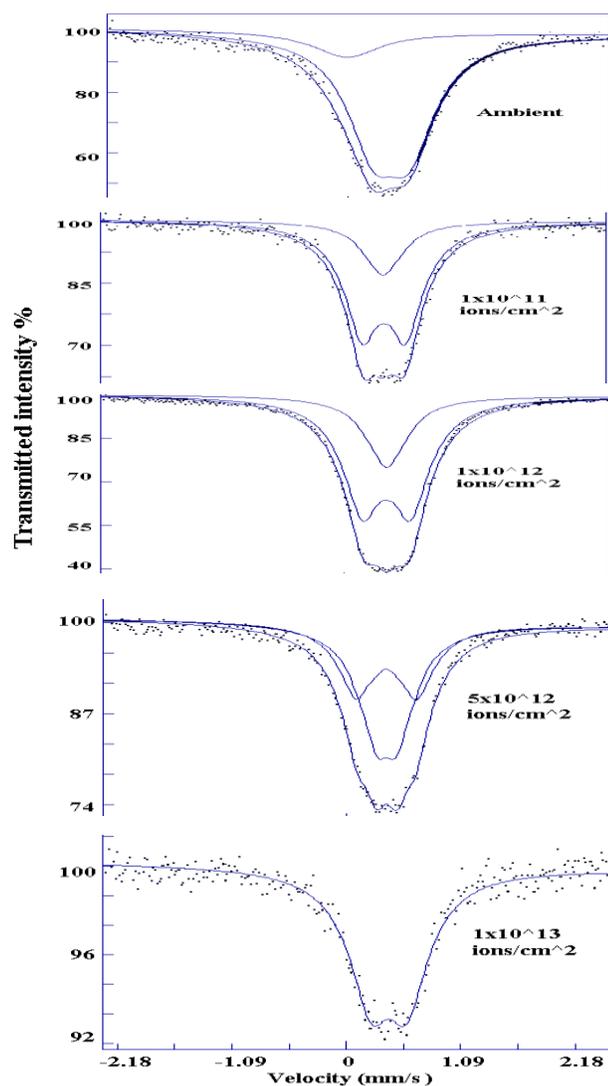
**Fig. 2.** XRD patterns of nanocrystalline stoichiometric  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$  sample at ambient condition and after SHI irradiation at various fluences using Fe-K $\alpha$  radiation. The peaks marked with \* are due to aluminum foil, also used for calibration of the patterns. The hkl values are also mentioned.



**Fig. 2 (A).** Comparison of XRD Patterns of unirradiated nanocrystalline stoichiometric  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$  sample, Mn-deficient and La-deficient samples using Fe-K $\alpha$  radiation. The peaks marked with \* are due to aluminum foil, also used for calibration of the patterns. The hkl values are also mentioned.



**Fig. 2 (B).** XRD pattern is taken of nanocrystalline  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$  sample irradiated at fluence of  $1 \times 10^{13}$  ions/cm<sup>2</sup> using CuK $\alpha$  radiation. The peaks marked with \* are due to aluminum foil, also used for calibration of the patterns. The hkl values are also mentioned.



**Fig. 3.** Room temperature Mössbauer spectra of SHI irradiated nanocrystalline stoichiometric  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$  sample at various fluence mentioned. The velocity scale is relative to metallic Fe.

The corresponding Mössbauer pattern of the nanocrystalline stoichiometric perovskite manganite represented by a paramagnetic doublet could be translated into two quadrupole splits doublets representing 15%  $\text{Fe}^{4+}$  ions in highly symmetric environment and 85% as  $\text{Fe}^{3+}$  ions present in the distorted octahedral environment. The presence of  $\text{Fe}^{4+}$  ions is reported for the first time in the system due to the sensitivity of the Mössbauer measurements [16]. High resolution Mössbauer spectroscopic measurements of irradiated sample at fluence of  $1 \times 10^{11}$  ions/cm<sup>2</sup> indicated an increase in isomer shift of one of the sites representing the transformation of  $\text{Fe}^{4+}$  ions into high spin  $\text{Fe}^{3+}$  ions. Similar effect was observed on application of hydrostatic pressure of 0.52GPa on the system [16].

**Table 2.** Room temperature Mössbauer Parameters of nano crystalline stoichiometric  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$  sample under various SHI irradiation fluence values.

SHI Irradiation Fluence	Quadrupole splitting (mm/sec)	Isomer shift (mm/sec) wrt Metallic Fe	Line width (mm/sec)	Population %
Zero	0.312±0.004 0	0.371±0.002 -0.003	0.556±0.004 0.462±0.026	85.88±4.24 $\text{Fe}^{3+}$ 14.22±0.40 $\text{Fe}^{4+}$
$1 \times 10^{11}$ ions/cm <sup>2</sup>	0.371±0.003 0	0.354±0.002 0.348±0.004	0.387±0.004 0.405±0.009	77.60±0.45 $\text{Fe}^{3+}$ 22.40±1.18 $\text{Fe}^{3+}$
$1 \times 10^{12}$ ions/cm <sup>2</sup>	0.405±0.001 0	0.359±0.0005 0.362±0.0009	0.422±0.002 0.421±0.002	73.91±0.83 $\text{Fe}^{3+}$ 26.09±0.09 $\text{Fe}^{3+}$
$5 \times 10^{12}$ ions/cm <sup>2</sup>	0.519±0.005 0.186±0.004	0.344±0.003 0.348±0.002	0.392±0.007 0.401±0.005	43.08±1.37 $\text{Fe}^{3+}$ 56.92±1.81 $\text{Fe}^{3+}$
$1 \times 10^{13}$ ions/cm <sup>2</sup>	0.315±0.008	0.371±0.005	0.480±0.010	100 $\text{Fe}^{3+}$

Isomer shift (IS) is a measure of s electron density at the Fe site therefore higher IS implies (a) extra 3d shielding lowering s electron density at the Fe nucleus and (b) electron transfer from a non-bonding ligand level to an antibonding 3d level of iron. Irradiation permits the thermal transfer of an electron from ligand to metal. The assignment of Fe in the two sites represented by different quadrupole splitting values is carried out according to the proposition proposed by Kopcewicz [25] considering the positions of Fe ions in the lattice differing in the orbital dynamics of their Mn environments ( $\text{Mn}^{3+}$  is Jahn-Teller ion while  $\text{Mn}^{4+}$  is non Jahn-teller ion). Doublet with large quadrupole splitting (QS) represented Fe position in which non Jahn Teller  $\text{Fe}^{3+}$  ions are octahedrally bonded to six  $\text{Mn}^{3+}$  ions whereas at the higher symmetric Fe position (lower quadrupole splitting) at least one manganese ion surrounding the Fe position should be in  $\text{Mn}^{4+}$  / vacancy state. It was also reported that the quadrupole splitting is sensitive to the oxygen environment. Increase in oxygen content is represented by a decrease in QS. Up to the fluence of  $1 \times 10^{12}$  ions/cm<sup>2</sup>, the site with higher QS is more populated indicating less vacancies but the situation drastically changes with further increase in the fluence of  $5 \times 10^{12}$  ions/cm<sup>2</sup> where the enhancement in the population of the doublet with higher symmetric site (lower QS) from 26% to 56% is observed indicating the increment in the  $\text{Mn}^{4+}$  ions/ vacancy in the system. The increase in quadrupole splitting in both the sites also might suggest the

decrease in oxygen content. The observed results support the earlier observation of vacancy creation at Mn-site through XRD. At irradiation of  $1 \times 10^{13}$  ions/cm<sup>2</sup>, both the sites merges into one doublet with little larger line width supporting the amorphous phase interpretation of XRD measurements. The uniform environment of a single doublet might arise from the ferromagnetic ordering by the introduction of non Jahn-Teller Fe<sup>3+</sup> ion in the Mn environment [25].

The effect of Fe doping on magnetization has been studied extensively. The magnetic moment decreases almost linearly with Fe doping [17]. Fe doping does not affect the lattice structure but it weakens the local ordering due to Mn atoms resulting into ferromagnetic ordering. Fig. 4 shows Magnetization versus Magnetic field (B-H) curves at 20 K on both pristine and irradiated sample with the fluence  $5 \times 10^{12}$  ions/cm<sup>2</sup>.

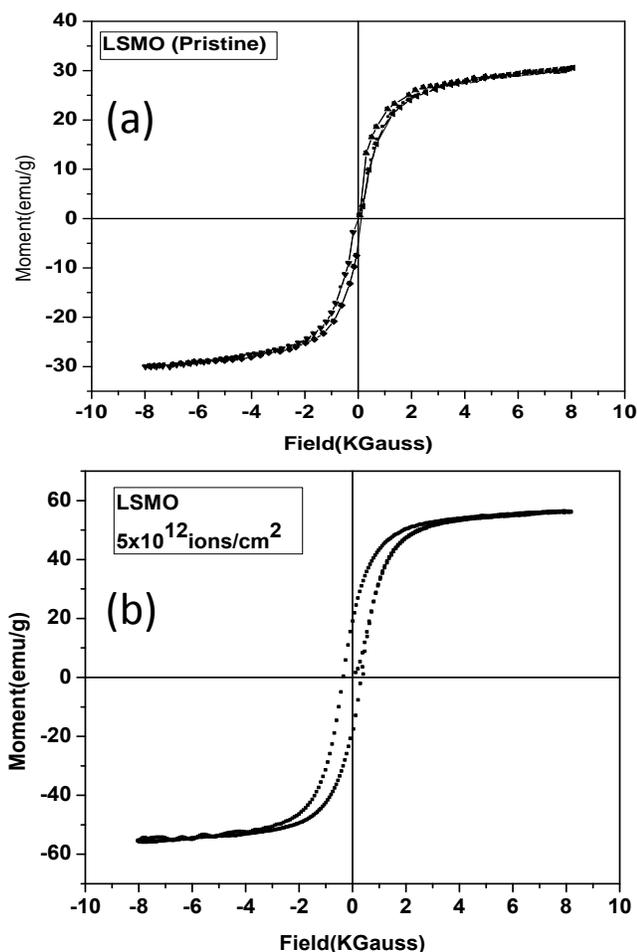


Fig. 4. Comparison of BH curves of pristine (a) and (b) irradiated with  $5 \times 10^{12}$  ions/cm<sup>2</sup> of nanocrystalline stoichiometric  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$  sample at 20 K.

The unirradiated nano-crystalline sample  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$  showed a constriction at  $H=0$  and this behavior at 20K might be attributed to the strong interaction between segregated Mn and Fe submicroscopic clusters. Enhanced magnetic moment observed along with increase in coercivity on irradiation confirmed single domain nature. Enhanced saturation magnetization on irradiation might be due to the modification induced on the surface states. Above results could also be explained based

on change of O ion environment which also affect the local electronic structure of Fe and Mn ions.

Occurrence of ferromagnetism and metallic behavior in manganite perovskites have been well explained by double exchange, mechanism through the hopping of an electron from Mn<sup>3+</sup> to Mn<sup>4+</sup> via oxygen, double exchange and superexchange interaction control the ferromagnetism in these systems. Chemical-doping, hydrostatic pressure promoted the ferromagnetic ordering reflecting the competition between super and double exchange. Swift heavy ions deposit high density of electronic energy and drive the material far from equilibrium causing unique modifications which is difficult to achieve by other means. It is known that the irradiation of oxide materials by swift heavy ions can result in different effects in materials such as defect annealing and defect creation depending upon the nature of ion beam, energy and fluence.

## Conclusion

Unlike bulk perovskites, the nanocrystalline systems seem to be sensitive to pressure and irradiation. The effect of irradiation due to SHI radiation with  $\text{Ag}^{+16}$  ions on stoichiometric nanocrystalline sample  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$  at various fluence studied using XRD, magnetic and Mössbauer spectroscopic techniques show no apparent structural phase transformation while structural transformation from orthorhombic to monoclinic phase was observed under hydrostatic pressure at 3.6 GPa. The low fluence of  $1 \times 10^{11}$  ions/cm<sup>2</sup> show similarity with low hydrostatic pressure of 0.52GPa by changing the valence of Fe<sup>4+</sup> to high spin Fe<sup>3+</sup> ion. Up to fluence  $5 \times 10^{12}$  ions/cm<sup>2</sup>, the nanocrystalline orthorhombic character is retained with creation of vacancies in the lattice. The increase in local lattice temperature at fluence  $1 \times 10^{13}$  ions/cm<sup>2</sup> causes randomization of the crystallites in the system indicated by broad smudged peaks. High resolution Mössbauer spectroscopic analysis supports XRD results of the vacancy formation by sharp increase in the population at the fluence  $5 \times 10^{12}$  ions/cm<sup>2</sup> and with uniform environment about Fe ions at fluence  $1 \times 10^{13}$  ions/cm<sup>2</sup>. The quadrupole splitting suggest Mn<sup>4+</sup> / vacancy creation and change in oxygen environment in the system due to irradiation. Such behavior in stoichiometric sample could be explained using double exchange mechanism in terms of complete ferromagnetic coupling between different Mn environments surrounding Fe ions. Enhanced magnetization also supports the proposition. While XRD and Magnetic measurements show the macroscopic behavior of the sample under the effect of irradiation, Mössbauer spectroscopic analysis indicates the microscopic dynamic behavior under the same conditions. The studies on vacancy-doped nanocrystalline (La,Sr)(Mn,Fe)O perovskites under irradiation would be interesting to understand the behavior of the system.

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