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A study on swift heavy ion irradiated nano-crystalline Li-Mg ferrite thin film

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Abstract : We have studied swift heavy ion (190 MeV Au^{14+}) induced defects in the nano-crystalline ferrite thin films, which has not been studied in detail yet. The system selected here is $Li_{0.25}Mg_{0.5}Mn_{0.1}Fe_{2.15}O_4$, which has its application as microwave devices in bulk. This film is deposited on Si(100) substrate by R. F magnetron sputtering technique. The film is annealed at 800°C under oxygen atmosphere after deposition. The XRD peaks are single phase and polycrystalline in nature with the crystals oriented towards (422) axis. From XRD pattern the grain size determination has been done. Elastic recoil detection analysis, resistivity measurement, X-ray diffraction measurement and conversion electron Mössbauer spectroscopy of the film is done to observe the damage creation in the system. A decrease in the value of resistivity with fluence, transition from ferrimagnetic state to paramagnetic state, broadening of peaks and no oxygen loss in the system reveals the existence of induced defects. The explanations are given on the basis of irradiation models. Following the condition used in this experiment the probability of formation of tracks and bursting of the grains are expected to be the relevant reasons for the damages.

Keywords : Nanocrystalline ferrites, heavy ion irradiation, oxygen content, resistivity, paramagnetic doublet, damage creation

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1. Introduction

Importances of nano-crystalline materials are increasing due to their versatile applications in the field of ferrites, semiconductors, chemical physics and biophysics. Basic difference between nanoparticles and bulk arises due to the fundamental properties, like small volume, high surface to volume ratio and grain boundaries comparable to grains. Many routine works have been done on nanopowders of ferrites to measure the magnetic, optical and other properties. In each case, special features are observed with decrease in particle size like decrease in saturation magnetization, change in Curie temperature, appearance of superparamagnetism and spin canting. We have taken the effort of preparing nano-crystalline ferrite thin films by radio frequency magnetron sputtering technique. Some ferrite films like Cu, Li are already prepared by some material scientists. Again a great change is observed in thin films from bulk. The applications of ferrite thin films are increasing in the field of recording media due to their extraordinary magnetic properties. Nowadays main emphasis is given on tailoring the properties of ferrite thin films to get a control over its application. We have tried to explore the tailoring by damage creation in the system. We are pioneering in tailoring the properties of nanoferrite thin films by heavy ion induced defects. The swift heavy ion irradiation is done in the system to induce defects. Heavy ion irradiations of magnetic insulators have been extensively studied since last two decades [1–3]. The importance of our work lies in the fact that defects are induced in the nanocrystalline materials. Swift heavy ions of high energy (MeV or GeV order) are of great interest for the study of electronic energy loss and its various effects. The heavy ions interacting with matter loses their energy either by inelastic collisions with electrons or by elastic collisions with nuclei. For high energy ions (here 190 MeV Au) the inelastic collisions are dominated with higher electronic stopping power (S_e) than nuclear stopping power (S_n). Many irradiation works have been done on ferrites like $MgFe_2O_4$, $ZnFe_2O_4$, $NiFe_2O_4$, garnets and hexaferrites. In most of the cases the ion-induced defects are well reflected in the magnetic properties. Specially the irradiation induced magnetization and rotation of internal field has become known phenomena for few ferrites. Some measures are taken to elucidate the radiation effects of SnO_2 nanopowders showing the disappearance of the finer grains [4]. Some years before Shinde *et al* suggested that nanoparticles are radiation hard in nature [5]. Following the above survey our experimental results showed tailoring can be done on nanoparticles by heavy ion irradiation on the contrary to Shinde *et al*. The system chosen by us is $Li_{0.25}Mg_{0.5}Mn_{0.1}Fe_{2.15}O_4$ and 190 MeV Au^{14+} ions are considered as heavy energy projectiles. A controlled defect can be formed controlling the fluences. From

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all the previous works we have seen if electronic stopping power is much higher than its threshold value then the electronic excitations result in the formation of latent tracks. In last few decades, many scientists have used high-resolution microscopy to observe the tracks directly. So the conditions of track formation are not unknown to us. Ion spike and thermal spike models can explain the detailed mechanism of track generation. The heat conduction mechanism being different than bulk in nano in some cases thermal spike may dominate. In fact this explanation is yet to explore. Thermal spike (TS) model is expected to correlate the nanoparticle irradiation with its fundamental properties. The heavy ions while passing through the matter excite the electronic subsystem, which consequently increases the temperature of the system *via* electron-electron and electron-phonon interaction. So a generation of excess heat may take place in the system. Our oxide film has a probability of decrease in the oxygen content of the film with increase in fluence. The elastic recoil detection analysis (ERDA) is the best suitable technique [6] used here to measure oxygen content of the film. To get a control over the resistivity online measurement is done with the increase in fluence. Similarly the conversion electron Mössbauer spectroscopy is used to observe the magnetic property of the system before and after irradiation. Presently, we are intending to explain the changes observed in nanoparticles on the basis of irradiation models. The online measurements are done at 15MV Pelletron accelerator at NSC.

2. Experimental outline

2.1. Thin film preparation :

Nanocrystalline thin films of $Li_{0.25}Mg_{0.5}Mn_{0.1}Fe_{2.15}O_4$ are deposited on Si (100) substrate using high pressure R.F magnetron sputtering technique. The sputtering is carried out in a custom built chamber using a 200 mm long, axial, planar magnetron source. The sputtering target is a sintered disc (50 mm diameter) prepared by standard ceramic technique placed about 5 cm away from the substrate. The base pressure is better than 1×10^{-6} Torr, while sputtering was carried out in the presence of a mixture of flowing argon and oxygen. After deposition annealing is done in oxygen atmosphere at 800°C for 3 hours. From XRD pattern the crystallite size is calculated following Debye-Scherrer equation [7] and it has come out nearly 20–25 nm.

2.2. Online measurements :

These films are mounted in a ladder inside the Goniometer chamber. Goniometer movement is used to bring the sample along the beam direction one by one. Different fluences are given to the films and online ERDA is done at N.S.C materials science beam line. The beam spot is confined to approximately 1 mm by 1 mm by the use of two double slits located before the chamber. The experimental set up consists of the detector, the goniometer and the gas chamber containing isobutane and related electronics. To increase sensitivity and therefore to avoid radiation damage of the films a detector with large solid angle is needed. With the increase in counts it is accompanied by decrease in resolution of the detecting system. Thus to achieve a suitable combination of high resolution and high-count capability a detector should be position sensitive. Position sensitivity is also important for eliminating the kinematic broadening. So a large angle position sensitive detector telescope (LAPSDT) is used. The detector telescope used here is gas ionization chamber. We need to detect all the elements, present in the films, so we do not use any stopper foil. A collimated beam of 190 MeV Au ions is incident on the ferrite films. The detector with the entrance window, made up of 1.5 µm polypropylene foil in front of it, is placed at an angle of 45° with respect to the beam.

A two-probe resistivity measurement is done using electrometer with increase in fluence.

2.3. CEMS measurement :

A conversion electron Mössbauer spectroscopy is done on the unirradiated and irradiated sample. The source used here is 25 mCi with Co^{57} placed in rhodium matrix.

3. Results and discussion

To measure the oxygen content of the film ERDA is used online. It determines all the elements simultaneously which helps to find out the ratio of O/Fe. The counts obtained for O and Fe are accumulated throughout the experiment with increase in fluence. Data is collected using "freedom" software developed at NSC. Event by event data is recorded which allows replay and manipulation. Finally, we obtain Figure 1 where we could not observe any measurable change in the oxygen content of the system. So the ratio may be considered as nearly constant through out the experiment.

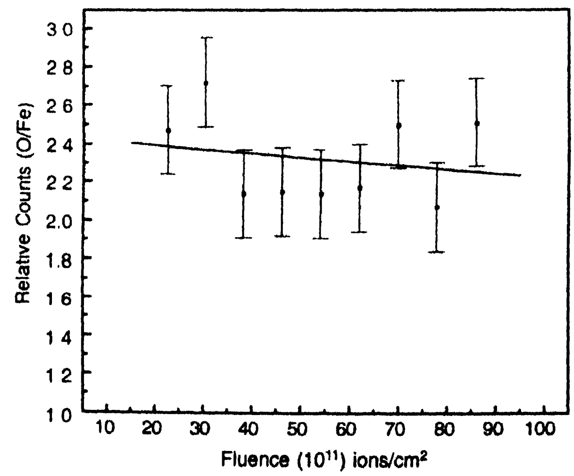
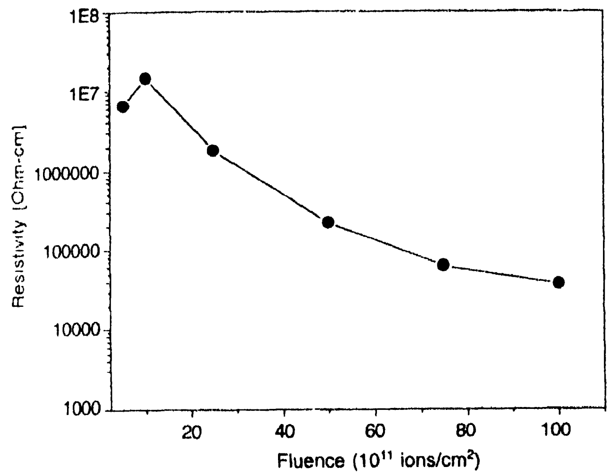


Figure 1. Relative counts of O/Fe with increase in fluence film annealed at 800°C.

Observation of electrical property like resistivity after irradiation is taken *in situ* by two-probe electrometer at different fluences. The resistivity of the pristine sample is $2.5 \times 10^5\ \Omega$ cm and after it is irradiated at 5×10^{11} ions/cm^2 the resistivity has increased to 6.3×10^6 Ω cm. Then for 10^{12} ions/cm^2 it starts decreasing with fluence. This nature is rather anomalous. The decrease in resistivity reveals the damage is created in the system due to heavy ions. Thus the insulating property of the ferrite thin films is decreasing with irradiation at higher fluences.

The conversion electron Mössbauer spectroscopy measurement on the thin film shows a drastic transformation from a ferromagnetic state to nearly complete paramagnetic state. This transition is observed at 2.5×10^{12} ions/cm^2 fluence. The appearance of paramagnetic doublet shows the heavy ion induced defects occurs after irradiation. The spectrum is shown in Figure 4.



'igure 2. Resistivity *vs* fluence when irradiated with 190 MeV Au^{14+} ions

The above-mentioned evidences are sufficient to establish he fact that nanocrystalline materials are not always radiation ard. All these effects are observed when the electronic topping power is much more than its threshold value. The bove condition is considered as the main factor, which create atent tracks. Many scientists have proved this phenomenon reviously. Various models have explained these track ormations. Mostly the explanations have been done by TS nodel. The resistivity and oxygen content measurement are new o the ferrite films. The resistivity data is most likely to follow TS nodel. In TS model the energy loss of heavy ions takes place fter the momentum transfer of the target electrons to the lattice ites by electron-electron and electron-phonon interactions. This inally lead to a molten zone with higher recombination time vhich results in the track formation. The heat generated hermalizes the bound electrons along the periphery. These hot lectrons in the conduction band acts like the hot electrons in he conduction band of metals [8]. The energy spreads stops vhen the electron energy becomes smaller than the ionization ne. For this measurement the diffusion parameter is most mportant which also determines the electron-phonon coupling actor. If we consider that there is no volume expansion due to rradiation then increase in temperature may account for the ncrease in pressure [9]. Therefore, this pressure along the ion path consequently give rise to a large shear force or shock waves which may be responsible for the defect creation in the lattice sites. This may decrease the resistivity of the system. As the crystals are nano in order so we cannot neglect the grain boundary effects. It might be possible that the dislocations are affected. This may result to the migration of high angle boundaries, which are much more mobile, over low angle boundaries. This decrease in resistivity can be well explained by polaron hopping conduction mechanism but the probability of formation of point defects are very less in this case. Formation of some localized stable bands below the conduction band may be formed which increases the conductivity of the system.

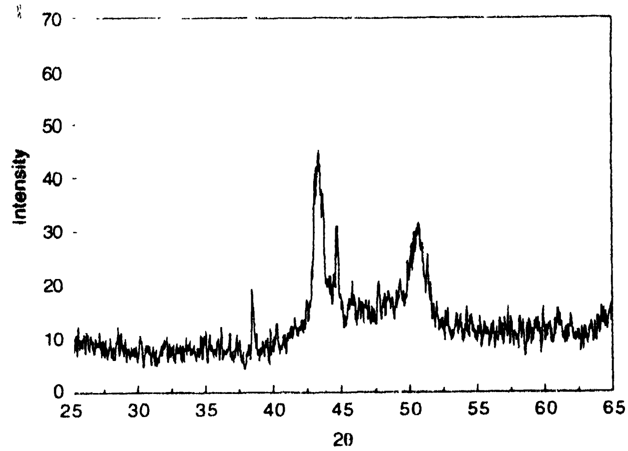


Figure 3. XRD pattern after irradiation with 5* 10^{12} ions/cm^2.

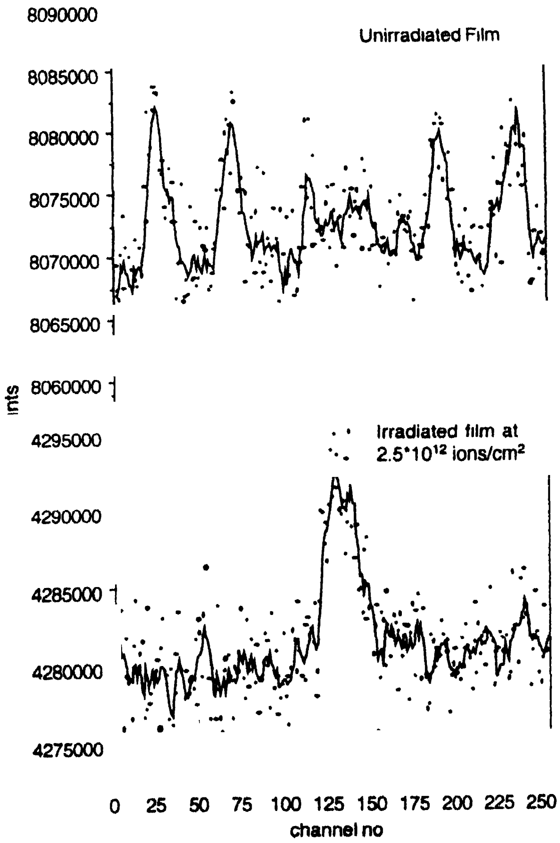


Figure 4. Conversion Electron Mössbauer Spectroscopy showing the swift heavy ion induced defects in the films.

Formation of paramagnetic doublet (as in our film) is also seen in some YIG and hexaferrites. The basic reason is considered to be track formation. But this phenomenon can be better explained by ion spike than thermal spike and the analysis is still going on.

To summarize we can say that as the heat generated is not decreasing the oxygen content of the system it may be confined in the small volume of nanoparticles. The heavy ions passing through the matter may burst into further finer grains. The X-ray diffraction pattern also agrees with this idea, which shows a broadened peak. With lower particle sizes considering the grain boundaries, as mentioned earlier, the resistivity can be decreased. The magnetic data also agrees with the formation of further nanograins. This represents the grains are below the critical size, which is showing more relaxation time.

4. Conclusion

The heavy ions can strongly tailor the properties of our film. A damage creation is taking place in the form of tracks and it is affecting the electrical and magnetic properties. The electrical property can mostly be explained by thermal spike generation. The overall experimental evidences are agreeing with the bursting of grains. Thus with fluence a controlled defect can be obtained which may control the external properties. We want to conclude the fact that nanoparticles are not always radiation resistant.

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