Nuclear Instruments and Methods in Physics Research B 379 (2016) 235–241

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Swift heavy ion irradiated spinel ferrite: A cheap radiation resistant material

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ARTICLE INFO

Article history:
Received 31 October 2015
Received in revised form 4 February 2016
Accepted 25 March 2016
Available online 1 April 2016

Keywords:
Ferrites
Cation distribution
In-situ X-ray diffraction
Ion irradiation
SEM

ABSTRACT

Effect of (80 MeV) ^{16}O 6^{+} ion irradiation on the structural properties and cation distribution of the as-burnt samples (i.e. the samples are without any thermal/sintering treatment) with the following compositions: $MnFe_2O_4$, $Mn_{0.5}Zn_{0.5}Fe_2O_4$ and $ZnFe_2O_4$ prepared by sol–gel auto-combustion technique have been studied through in-situ and ex-situ X-ray diffraction (XRD) technique. Well characterized single phase $MnFe_2O_4$ and $Mn_{0.5}Zn_{0.5}Fe_2O_4$ samples were irradiated at fluence 1×10^{11}, 1×10^{12}, 1×10^{13} and 1×10^{14} ions/cm^2 to see the effect of the electronic energy loss induced changes in the structural properties and in cation distribution monitored through ex-situ XRD. $ZnFe_2O_4$ samples were irradiated with ion fluence values ranging between $1 \times 10^{11} - 2 \times 10^{14}$ ions/cm^2 to observe the effect of in-situ XRD on structural properties and cation distribution. Results very clearly depict the redistribution of cations in the samples, which show noticeable changes in: ionic radii of A-site ($\boldsymbol{r_A}$) and B-site ($\boldsymbol{r_B}$), experimental and theoretical lattice parameter ($\boldsymbol{a_{exp.}}$, $\boldsymbol{a_{th.}}$), unit cell volume ($\boldsymbol{V}$), Scherrer's Grain diameter ($\boldsymbol{D}$), oxygen positional parameter ($\boldsymbol{u}$), tetrahedral and octahedral bond length ($\boldsymbol{R_A}$, $\boldsymbol{R_B}$), shared tetrahedral and octahedral edge ($\boldsymbol{d_{AE}}$, $\boldsymbol{d_{BE}}$) and bond angles (θ_1, θ_2, θ_3, θ_4, θ_5). Results are interpreted in terms of irradiation induced changes in the above mentioned parameters.

1. Introduction

Swift heavy ion (SHI) irradiation is known to generate controlled defects, which can alter the structural properties, cation distribution and can produce strain/stress in the lattice. The observed structural effects induced via SHI irradiation depends on the mechanism of ion material interaction, type of ion beam, its energy, material composition [1] and on the ferrite structure. From structure point of view, several effects can be induced due to swift heavy ion irradiation of the material: increase of lattice parameter, change of site, amorphisation, creation of tracks showing either elongated extended defects or continuous amorphous cylinders [2]. The swift heavy ions during their passage through the materials lose their energy by two processes; by inelastic collisions with the electrons (electronic energy loss S_e) and by elastic collisions with the nuclei (nuclear energy loss S_n). For heavy ions in the mega electron volt range (MeV), the electronic energy loss dominates over the nuclear energy loss and is able to generate various types of defects such as point/clusters and columnar defects depending upon the magnitude of S_e. To create columnar defects, certain threshold value of electronic energy loss (S_{eth}) is required. If S_e is less than the S_{eth}, it will create only point or clusters of defects [3]. The SHI stimulated defects are known to create structural strain and disorder in ferrites and are responsible to modify their properties. Efforts have been made to improve the performance of ferrites in electronic components used in highly radioactive environment such as in nuclear facilities, even in the satellites and space craft's [4–6].

Ferrites are important magnetic materials having spinel structure and considered to be better candidates for spintronic devices, magnetic drug delivery, in radioactive environment and in space applications, when synthesized in nano regime [5,7–9]. SHI can be used as an alternate tool for designing materials with new structural and magnetic properties by changing the structure of the materials by producing different types of defects [10,11]. Investigations on the irradiation of spinel ferrites are of interest in several fields, e.g. behavior of ferrites near a reactor, in space station and in the nuclear industries where nano-porous material can be used because they act as a perfect sinks for defects and has the potential to be extremely radiation tolerant [2,5,12]. During past few years, various radiation effects on the structural and magnetic properties of ferrites with different compositions have been studied [13–19],

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http://dx.doi.org/10.1016/j.nimb.2016.03.052
0168-583X/

but according to the authors best knowledge no detailed study is available on the in-situ and ex-situ X-ray diffraction (XRD) studies of SHI irradiation of the ferrite nano-particles.

Therefore, in the present work we report the studies on the SHI effect of 80 MeV (2 particle nano Ampere (pnA) [*1 pnA is the measured current during irradiation per charge state of the ion*]) $^{16}O\ 6^{+}$ ion irradiation on the structural properties, and cation distribution of the as-burnt samples, monitored through ex-situ and in-situ XRD with the following compositions: $MnFe_2O_4$, $Mn_{0.5}Zn_{0.5}Fe_2O_4$ and $ZnFe_2O_4$.

2. Experimental details

Powders with nominal composition $Mn_{1-x}Zn_xFe_2O_4$ ($x = 0, 0.5, 1.0$) were prepared by sol–gel auto-combustion technique as described elsewhere [20], using citrate–nitrate precursors as sources of metals and citric acid as fuel. Sol–gel auto-combustion is one of the most efficient method, for preparing nano-materials under moderate conditions where, one can have the final phase formation even in ‘dry gel’ form, so no further sintering would be needed [20–22]. In nano-materials, grain and inter-phase boundaries act as point-defect sinks reducing damage accumulation and possible swelling, which makes it fascinating for its prospective use as a cheap radiation shield in nuclear reactors. In the case of nanoparticles, the surface to volume ratio is high; the surface energy plays a major role in their structural and physical properties and can be modified by SHI irradiation. In-situ and ex-situ XRD measurements were done at room temperature in $\theta-2\theta$ configuration by Bruker D8 advance diffractometer utilizing CuK_α ($\lambda = 0.1540562$ nm) radiation. Advantage of in-situ XRD over ex-situ XRD lies in its ability to directly monitor the structural changes occurring in the material during irradiation. Experimental lattice parameter ($\boldsymbol{a_{exp.}}$), unit cell volume ($\boldsymbol{V}$), X-ray density ($\boldsymbol{\rho_{XRD}}$), Scherrer’s Grain diameter ($\boldsymbol{D}$) of the studied samples were calculated as described in [20]. Cation distribution of the studied samples was estimated using X-ray diffraction intensities. The calculated and observed intensity ratios were compared for several combinations of cation distribution at tetrahedral (A) and octahedral [B] sites as described in [23]. The best cation distribution among A and B sites for which theoretical and experimental intensity ratios agree clearly, is taken to be the correct one. With the help of obtained cation distribution, ionic radii of A-site ($\boldsymbol{r_A}$) and B-site ($\boldsymbol{r_B}$), theoretical lattice parameter ($\boldsymbol{a_{th.}}$), oxygen positional parameter ($\boldsymbol{u}$), tetrahedral and octahedral bond length ($\boldsymbol{R_A}$, $\boldsymbol{R_B}$), shared tetrahedral and octahedral edge ($\boldsymbol{d_{AE}}$, $\boldsymbol{d_{BE}}$) and the bond angles ($\boldsymbol{\theta_1}$, $\boldsymbol{\theta_2}$, $\boldsymbol{\theta_3}$, $\boldsymbol{\theta_4}$, $\boldsymbol{\theta_5}$) were calculated as described in [24–26]. Error in the estimation of the X-ray parameters is standard deaviation and is mentioned as follows: lattice parameter- ±0.003 nm, cell volume- ±0.007 nm^3, ionic radii of A-site and, B-site- ±0.003 nm and 0.001 nm, oxygen positional parameter- ±0.002, bond lengths and shared etrahedral/octahedral edge is ±0.003 nm/±0.002 nm and, for Scherrer’s grain diameter it is ±1.2 nm. It should be noted that reported values of XRD parameters in Tables 1 and 2 are out of error bar, except Scherrer’s grain diameter. The morphological behavior of the un-irradiated samples were determined by using scanning electron microscopy (SEM) technique (FEI Quanta 400FEG). $MnFe_2O_4$, $Mn_{0.5}Zn_{0.5}Fe_2O_4$ and $ZnFe_2O_4$ samples (without any post-preparation thermal/sintering treatment) were irradiated with 80 MeV $^{16}O\ (6^{+})$ ion using 15 UD Pelletron Accelerator at Inter University Accelerator Centre, New Delhi. The ion beam current was about 2 pnA. $MnFe_2O_4$ and $Mn_{0.5}Zn_{0.5}Fe_2O_4$ were irradiated at fluence 1×10^{11}, 1×10^{12}, 1×10^{13} and, 1×10^{14} ions/cm^2. Structural modifications induce via SHI irradiation were monitored using ex-situ XRD. $ZnFe_2O_4$ samples were irradiated with ion fluence ranging between $1 \times 10^{11} - 2 \times 10^{14}$ ions/cm^2. Structural changes in Zn ferrite samples were observed using in-situ XRD.

3. Results and discussions

3.1. SRIM calculations

From SRIM – The Stopping and Range of Ions in Matter calculation [27] Code, the electronic energy loss (S_e), nuclear energy loss (S_n) and projected range (R_p) for $MnFe_2O_4$, $Mn_{0.5}Zn_{0.5}Fe_2O_4$ and $ZnFe_2O_4$ were calculated using density 5.0919 g/cm^3, 5.1904 g/cm^3, 5.4024 g/cm^3 respectively. S_e of 80 MeV $^{16}O^{6+}$ ion in $MnFe_2O_4$, $Mn_{0.5}Zn_{0.5}Fe_2O_4$ and $ZnFe_2O_4$ is 1.577×10^2, 1.59×10^2 and 1.646×10^2 eV/A respectively, S_n of 80 MeV $^{16}O^{6+}$ ion in $MnFe_2O_4$, $Mn_{0.5}Zn_{0.5}Fe_2O_4$ and $ZnFe_2O_4$ is 9.436×10^{-2}, 9.59×10^{-2} and 9.954×10^{-2} eV/A respectively and R_p of 80 MeV $^{16}O^{6+}$ ion in $MnFe_2O_4$, $Mn_{0.5}Zn_{0.5}Fe_2O_4$ and $ZnFe_2O_4$ is 36.99, 36.73 and 35.72 µm respectively. For all the three different compositions,

Table 1
Irradiation dose (ions/cm^2) dependence of experimental and theoretical lattice parameter ($\boldsymbol{a_{exp.}}$, $\boldsymbol{a_{th.}}$), cell volume ($\boldsymbol{V}$), (%) change in $\boldsymbol{V} - \boldsymbol{\Delta V}$, ionic radii of A-site ($\boldsymbol{r_A}$) and B-site ($\boldsymbol{r_B}$) and average grain diameter ($\boldsymbol{D}$) of pristine and irradiated $Mn_{1-x}Zn_xFe_2O_4$ ($x = 0.0, 0.5, 1.0$) system.

Dose	Cation distribution	$\boldsymbol{a_{exp.}}$ (nm)	$\boldsymbol{a_{th.}}$ (nm)	$\boldsymbol{V}$ (nm^3)	$\boldsymbol{\Delta V}$ %	$\boldsymbol{r_a}$ (nm)	$\boldsymbol{r_b}$ (nm)	$\boldsymbol{D}$ (nm)
x = 0.0 (Ex-Situ XRD)								
0	$(Mn^{2+}_{0.20}Fe^{3+}_{0.80})_A\ [Mn^{2+}_{0.80}Fe^{3+}_{1.20}]_B$	0.8442	0.8529	0.6016	0.00	0.0524	0.0719	10.04
1×10^{11}	$(Mn^{2+})_A\ [Fe^{3+}_2]_B$	0.8435	0.8541	0.6001	−0.25	0.0660	0.0645	9.39
1×10^{12}	$(Mn^{2+}_{0.20}Fe^{3+}_{0.80})_A\ [Mn^{2+}_{0.80}Fe^{3+}_{1.20}]_B$	0.8441	0.8529	0.6014	−0.03	0.0524	0.0719	8.18
1×10^{13}	$(Fe^{3+})_A\ [Mn^{2+}Fe^{3+}]_B$	0.8438	0.8525	0.6008	−0.14	0.0490	0.0738	9.98
1×10^{14}	$(Mn^{2+}_{0.05}Fe^{3+}_{0.95})_A\ [Mn^{2+}_{0.95}Fe^{3+}_{1.05}]_B$	0.8457	0.8526	0.6049	+0.55	0.0499	0.0733	8.77
x = 0.5 (Ex-Situ XRD)								
0	$(Mn^{2+}_{0.25}Zn^{2+}_{0.35}Fe^{3+}_{0.40})_A\ [Mn^{2+}_{0.25}Zn^{2+}_{0.15}Fe^{3+}_{1.60}]_B$	0.8451	0.8484	0.6036	0.00	0.0571	0.0675	14.06
1×10^{11}	$(Mn^{2+}_{0.25}Zn^{2+}_{0.50}Fe^{3+}_{0.25})_A\ [Mn^{2+}_{0.25}Fe^{3+}_{1.75}]_B$	0.8366	0.8491	0.5855	−2.99	0.0588	0.0668	10.01
1×10^{12}	$(Zn^{2+}_{0.40}Fe^{3+}_{0.60})_A\ [Mn^{2+}_{0.50}Zn^{2+}_{0.10}Fe^{3+}_{1.40}]_B$	0.8438	0.8483	0.6008	−0.46	0.0534	0.0696	12.52
1×10^{13}	$(Zn^{2+}_{0.40}Fe^{3+}_{0.60})_A\ [Mn^{2+}_{0.50}Zn^{2+}_{0.10}Fe^{3+}_{1.40}]_B$	0.8457	0.8483	0.6049	+0.22	0.0534	0.0696	14.85
1×10^{14}	$(Zn^{2+}_{0.50}Fe^{3+}_{0.50})_A\ [Mn^{2+}_{0.50}Fe^{3+}_{1.50}]_B$	0.8442	0.8487	0.6016	−0.33	0.0545	0.0691	12.25
x = 1.0 (In-Situ XRD)								
0	$(Fe^{3+})_A\ [Zn^{2+}Fe^{3+}]_B$	0.8400	0.8406	0.5927	0.00	0.0490	0.0693	15.38
1×10^{11}	$(Zn^{2+}_{0.70}Fe^{3+}_{0.30})_A\ [Zn^{2+}_{0.30}Fe^{3+}_{1.70}]_B$	0.8381	0.8436	0.5887	−0.67	0.0567	0.0655	18.23
3×10^{11}	$(Zn^{2+}_{0.60}Fe^{3+}_{0.40})_A\ [Zn^{2+}_{0.40}Fe^{3+}_{1.60}]_B$	0.8406	0.8431	0.5940	+0.22	0.0556	0.0664	16.02
1×10^{12}	$(Zn^{2+}_{0.85}Fe^{3+}_{0.15})_A\ [Zn^{2+}_{0.15}Fe^{3+}_{1.85}]_B$	0.8454	0.8442	0.6042	+1.94	0.0584	0.0662	14.70
3×10^{12}	$(Zn^{2+}_{0.40}Fe^{3+}_{0.60})_A\ [Zn^{2+}_{0.60}Fe^{3+}_{1.40}]_B$	0.8418	0.8423	0.5965	+0.64	0.0534	0.0674	17.80
1×10^{13}	$(Zn^{2+}_{0.80}Fe^{3+}_{0.20})_A\ [Zn^{2+}_{0.20}Fe^{3+}_{1.80}]_B$	0.8360	0.8439	0.5843	−1.42	0.0578	0.0655	15.59
3×10^{13}	$(Zn^{2+}_{0.70}Fe^{3+}_{0.30})_A\ [Zn^{2+}_{0.30}Fe^{3+}_{1.70}]_B$	0.8410	0.8436	0.5948	+0.35	0.0567	0.0659	16.70
1×10^{14}	$(Zn^{2+}_{0.90}Fe^{3+}_{0.10})_A\ [Zn^{2+}_{0.10}Fe^{3+}_{1.90}]_B$	0.8382	0.8447	0.5889	−0.64	0.0589	0.0650	16.19
2×10^{14}	$(Zn^{2+}_{0.60}Fe^{3+}_{0.40})_A\ [Zn^{2+}_{0.40}Fe^{3+}_{1.60}]_B$	0.8450	0.8431	0.6034	+1.81	0.0556	0.0664	11.93