J Mater Sci (2011) 46:2294–2299
DOI 10.1007/s10853-010-5071-6

Effect of γ-rays irradiation on the structure and magnetic properties of Mg–Cu–Zn ferrites

M. M. Eltabey · I. A. Ali · H. E. Hassan · M. N. H. Comsan

Received: 4 September 2010 / Accepted: 9 November 2010 / Published online: 24 November 2010

Abstract The effect of γ-irradiation on the structure and magnetic properties of ferrite samples with chemical formula $Mg_xCu_{0.5-x}Zn_{0.5}Fe_2O_4$ (where $x = 0.0$, 0.2, and 0.4) prepared by conventional ceramic method has been studied. X-ray diffraction patterns (XRDPs) indicated the presence of a single spinel phase for all the investigated samples. The initial permeability and magnetization were measured, before and after irradiation on toroidal samples used as transformer cores. The initial permeability μ_i was measured as a function of temperature at constant frequency of 10 kHz and Curie temperatures (T_C) were determined. It was found that, due to irradiation, both of lattice parameter and porosity were increased. On the other hand, the values of magnetization and initial permeability were decreased as a result of irradiation. In addition, there was a decrease in the crystallite size, homogeneity, and the values of Curie temperature with significant decrease in the values of μ_i and T_C for the sample with $x = 0.0$. The results are discussed in the light of γ-rays interaction with ferrite lattice.

M. M. Eltabey (✉)
Department of Basic Engineering Science, Faculty of Engineering, Menoufiya University, Shebin El-Kom, Egypt
e-mail: m.m.eltabey@gmail.com

I. A. Ali · H. E. Hassan · M. N. H. Comsan
Cyclotron Facility, Nuclear Research Center, Atomic Energy Authority, Cairo 13759, Egypt

H. E. Hassan
Physics Department, Faculty of Science, Taif University, Al-Hawiah, P.O. Box 888, Taif, Saudi Arabia

Introduction

The importance of different types of ferrites emerges from their applications in industry and electronic circuits [1]. With the rapid development of mobile communication and information technology, small, inexpensive, and high performance electronic devices are in high demand [2]. Recently, we have witnessed the fast development of surface mounting devices (SMD) in which multilayer chip inductors (MLCI) are used. Ni–Cu–Zn ferrites are employed as a magnetic material for MLCIs because of its suitable magnetic properties at high frequencies and its low sintering temperature [3]. Similarly, Mg–Cu–Zn ferrites found potentials in electronic industry with the advantages that they are economical and easy to synthesize [1]. Therefore, Mg–Cu–Zn ferrites are considered a promising material for MLCIs with high-performance and low cost [4]. Moreover, they are useful in the fabrication of cores of intermediate frequency transformers (IFT) for amplitude modulation [5].

The recent increasing in development of measuring devices and data acquisition modules in nuclear reactors and accelerators put forward more often the problem of the radiation effects on these electronic components. Even the satellites and space crafts can be exposed to cosmic radiation of rather high dose. The radiation may cause excitation, ionization of atoms, or disturbance in the structure of matter [6]. It was reported that, both the diffusion coefficient of oxygen ions and the lattice parameters were increased as a result of irradiation of Co-Zn ferrites by γ-rays [7]. The effect of γ irradiation on the dielectric properties, thermoelectric power and thermal conductivity of Co–Zn ferrites and on the electrical properties of Li–Co–Yb ferrites were studied [7–10]. In a recent study, it was found that the γ-rays irradiation improved the magnetic properties of Mg–Mn ferrites nano-particles [11]. In this study, the effect of γ-rays irradiation on the structure and magnetic properties of Mg–Cu–Zn ferrites with different compositions is studied. The influence of initial permeability and Curie temperature by irradiation is investigated.

Experimental

Samples of $Mg_xCu_{0.5-x}Zn_{0.5}Fe_2O_4$ ferrite system with $x = 0.0$, 0.2, and 0.4 were synthesized using conventional ceramic method. A mixture of MgO, CuO, ZnO, and Fe_2O_3, with purity 99.9%, was prepared in their respective stoichiometric ratio and milled using mechanical agate grinder. To start the primary reactions between the mixed oxides, the samples were presintered in muffle furnace at 900 °C for 30 h. The samples were ground again mechanically and pressed in toroidal die under uniaxial pressure of 4.7×10^8 Pa. They were finally sintered at 1050 °C for 10 h and slowly cooled to room temperature with cooling rate 1 °C/min. XRDPs were performed using a diffractometer of type X'Pert Graphics and identified with Cu Kα radiation. To calculate the porosity percentage of every sample, theoretical and apparent densities were determined. The theoretical X-ray density (d_x) of the samples was calculated using the formula $d_x = 8\ M/Na^3$, where, M is the molecular weight, N is Avogadro's number, and a is the lattice parameter. The density d of each composition was measured in distilled water using Archimedes principle. The porosity percentage P (%) was calculated according to the relation $P = 100[1 - (d/d_x)]\%$ [12].

Toroidal samples of average inner diameter 0.85 cm, outer diameter 1.7 cm, and thickness = 0.4 cm were prepared and used as transformer cores for measuring the initial permeability (μ_i) as a function of frequency at room temperature. To avoid the interference between the effect of heating and the effect of irradiation, we used one toroide for the temperature dependence of μ_i and another one for the frequency dependence for each composition. The primary coil, of 20 turns, was wounded around the toroide and connected to ac generator type BK-4040A. The induction voltage (V_s) at the secondary coil of 15 turns was measured using multimeter type BK-5492MH. The temperature of the sample was measured using thermocouple type K inserted in the toroide center and connected to digital thermometer type BK-710. Polotinnikov formula [13], $V_s = K\,\mu_i$, was used to determine the μ_i, where, K is constant related to the number of turns for the primary (n_p) and secondary coils (n_s), toroide cross-sectional area (A), average path of the magnetic flux (r_m), and the applied frequency f. The induced magnetization M in the toroidal samples by applying magnetic field H was determined from the relation $M = (B/\mu_0) - H$, where B is the magnetic flux, μ_0 is the air permeability, $B = 2500V_s/(10^4 A n_s f)$, $H = n_p i_p/(2\pi r_m)$, $r_m = (r_i + r_o)/2$, r_i is the inner radius and r_o is the outer radius of the toroidal sample [14]. The samples were exposed to γ-rays of ^{60}Co radioactive source in irradiation cell in Nuclear Research Center, Atomic Energy Authority, Cairo, Egypt. The dose was amounted 1.9 MGy with dose rate 5 KGy/h.

Results and discussion

X-ray analysis

Figure 1 shows the XRDPs of unirradiated and irradiated samples with $x = 0.0$, 0.2, and 0.4 of Mg-concentrations. All the XRDPs show single spinel phase for all investigated samples. The average crystallite size (D), as indicator to the grain size, was calculated using Debye–Scherer formula. It was found that the value of D is within the range 134–160 nm. XRDPs show that, a slight shift of the reflected peaks for the irradiated samples. The relative intensities of the peaks (400) and (533) decreased after irradiation for the un-substituted sample (with $x = 0$). Whereas, they increased in the substituted ones (samples with $x = 0.2$ and $x = 0.4$). Also, it is noticed that, for the un-substituted sample, the intensity of the peak (440) became greater than that of the (311) peak. These results reveal that after irradiation the plane (440) became more dense than (311) plane. Such results, the shift in the reflected peaks were in agreement with that reported by different authors and they attributed that to the distortion occurred in the cubic lattice after irradiation [15, 16]. Whereas the obtained modifications in the relative intensity

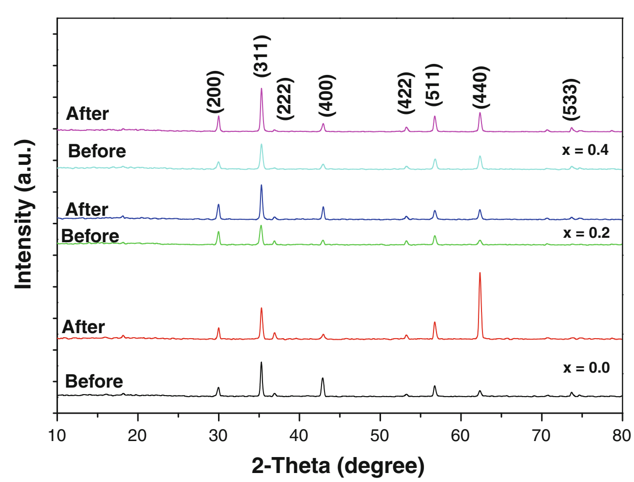

Fig. 1 XRDPs for $Mg_xCu_{0.5-x}Zn_{0.5}Fe_2O_4$ ferrites ($x = 0.0$, 0.2, and 0.4) before and after irradiation

of some reflecting planes due to the irradiation are quite differ from their results.

Lattice parameter

The *d*-spacing for each peak was recorded automatically and then the lattice parameter (*a*) was calculated from the relation $a = d_{hkl}(h^2 + k^2 + l^2)^{(1/2)}$. The values of lattice parameters obtained for each reflected plane are plotted against the function $F(\theta)$, where $F(\theta) = (1/2)[(\cos^2\theta/\sin\theta) + (\cos^2\theta/\theta)]$; θ is the Bragg's angle. Straight lines were obtained and the accurate values of (*a*) were determined from the extrapolation of these lines to $F(\theta) = 0$ [17]. The variation of lattice parameter with Mg-concentration before and after irradiation is illustrated in Fig. 2a. It is clear that, as Mg-concentration increases the lattice parameter decreases approximately linearly obeying Vegard's law. This result could be explained on the basis of the ionic radii due to the replacement of Cu^{+2} ions of larger ionic radius (0.72 Å) by the Mg^{+2} ions of smaller one (0.65 Å) [18]. Furthermore, it is obvious that the lattice parameters for the irradiated samples are larger than that of the unirradiated ones. This could be attributed to the formation of ferrous ion, Fe^{2+}, with radius (0.78 Å) which is larger than that of ferric ion, Fe^{3+} (0.64 Å). The formation of ferrous ions due to γ-rays irradiation of ferrites was reported by Refs. [6, 8–10, 15, 19, 20].

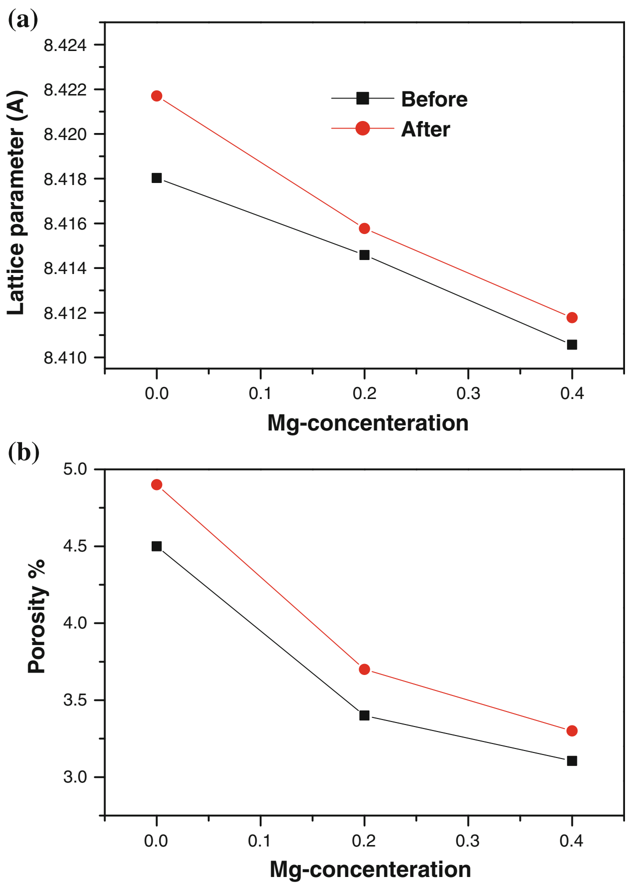

Fig. 2 **a** Lattice parameter versus content of Mg^{2+} ions before and after radiation. **b** Porosity versus content of Mg^{2+} ions before and after irradiation

Porosity

The variation of porosity (*P* %) with Mg-concentration, for the investigated samples before and after irradiation, is shown in Fig. 2b. One can observe that as Mg-concentration increases (*P* %) decreases. The result indicates that, the Mg-substitutions improve the densification of the ferrite. This behavior could be attributed to filling of the interstitial positions by the smaller Mg^{2+} ions, then increasing the density [18]. Also, it is noticed that, the values of porosity for the irradiated samples are higher than that of unirradiated ones. This increase in the porosity could be attributed to the generation of some lattice imperfections like voids or vacancies at different depths according to the interaction of γ-rays with matter [7, 9, 19].

Initial permeability and Curie temperature

Figure 3 shows the frequency dependence of the initial permeability for unirradiated and irradiated samples at room temperature. It is seen that, μ_i is approximately frequency independent over the measured frequency range. Also, the values of μ_i for the irradiated samples are lower than that of unirradiated ones. The composition dependence of μ_i is illustrated in Fig. 4a. It is obvious that, as Mg-concentration increases the value of μ_i decreases. The effects of both Mg-substitution and irradiation on the value of μ_i could be explained on the bases of domain theory. According to that theory, the initial permeability could be resolved into two types of mechanisms. They are: (1) contribution from spin rotation and (2) contribution from domain-wall motion [21, 22]. However, the contribution from spin rotation was found to be too smaller than that of domain-wall motion [23]. So, the permeability in ferrites is mainly due to domain-wall motion which is given by

$$(\mu_i - 1)_w \approx \frac{3\pi M_s^2 D}{4\Gamma} \quad (1)$$

where M_s is saturation magnetization, *D* is mean grain size, Γ is magnetic domain-wall energy, which is proportional to the global anisotropy constant [24, 25]. Thus, μ_i could be written as,

$$\mu_i \cong \frac{M_s^2 D}{K} \quad (2)$$

where *K* is magnetocrystalline anisotropy constant.

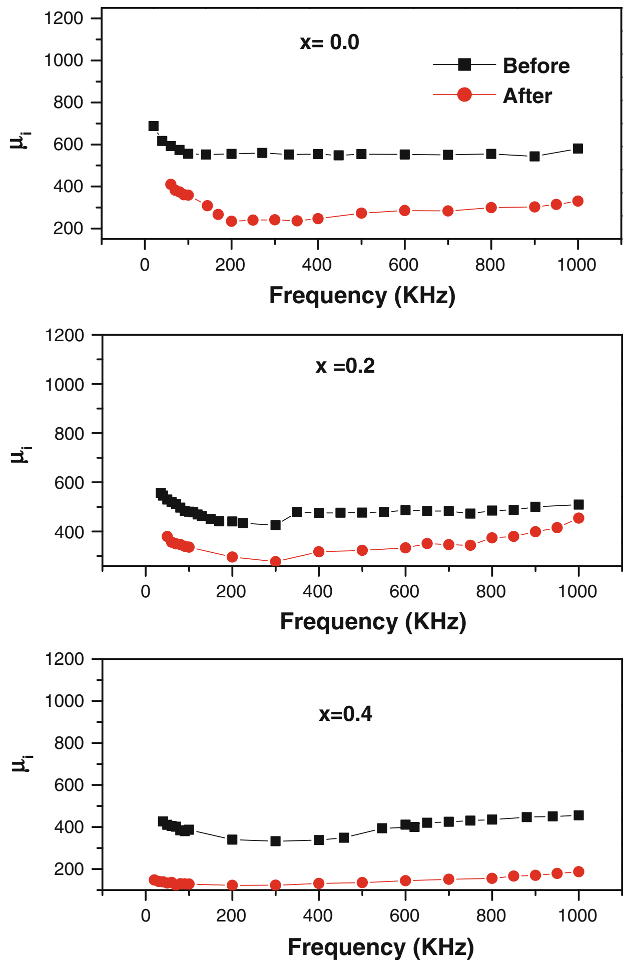

Fig. 3 The initial permeability versus frequency (KHz) of $Mg_x Cu_{0.5-x}Zn_{0.5}Fe_2O_4$ ($x = 0.0$, 0.2, and 0.4) before and after irradiation

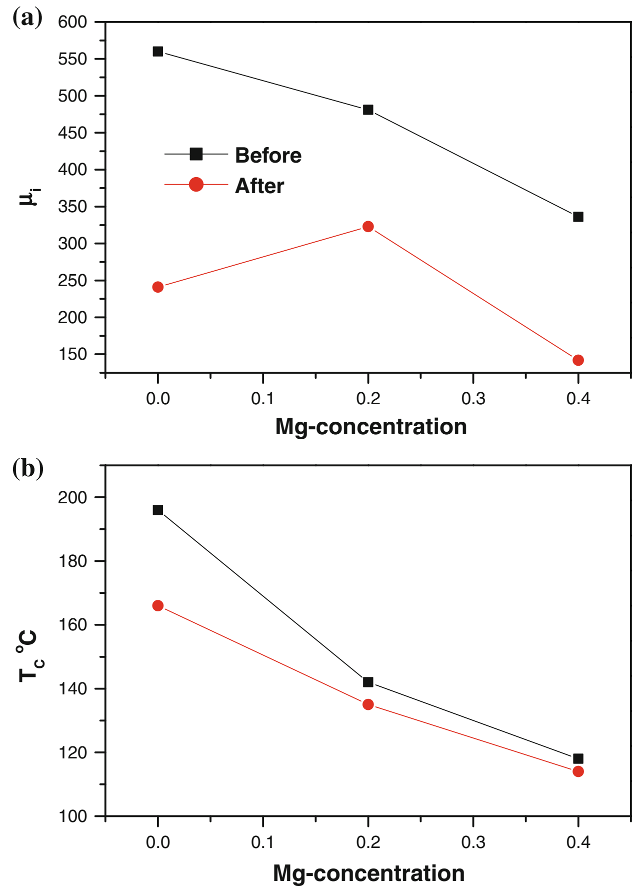

Fig. 4 **a** The initial permeability at $f = 400$ kHz versus content of Mg^{2+} ion before and after radiation. **b** Curie temperature versus content of Mg-concentration before and after irradiation

The behavior of μ_i with Mg-concentration could be explained in terms of Eqs. 1 and 2. The results given in Table 1 show that both magnetization and the average crystallite size decrease with increasing Mg concentration. From Eq. 2, this leads to decreasing in μ_i as Mg-concentration increases which is in agreement with the results reported by Yue et al. [4] and Rezlescu et al. [26]. This effect probably due to the replacement of Cu^{2+} ion of magnetic moment ($=1\ \mu_B$) by the non-magnetic Mg^{2+} ion [27], as both of them prefer the occupation of B-site [28]. On the other hand, the value of K (-2.5×10^{-4}) for $MgFe_2O_4$ composition is lower than that of $CuFe_20_4$ (-6×10^{-4}) [29, 30] leading to increasing of μ_i as Mg-concentration increases. Thus, the obtained behavior of μ_i versus Mg-concentration reveals that the effect of both M and D is more dominant than that of K.

From Table 1, it is clear that the average crystallite size was decreased by irradiation for all Mg-concentrations. This also, according to Eq. 2, caused a decrease in permeability of all the samples as shown in Fig. 4a. Similar behavior was reported for Co–Zn–Ce and Mg–Ti–Er ferrites irradiated by γ-rays [16, 18]. Furthermore, the magnetization decreased by irradiation for all the investigated samples. This could be attributed to the transformation of Fe^{3+} ions of magnetic moment ($5\ \mu_B$) to Fe^{2+} of lower magnetic moment ($4\ \mu_B$), due to the effect of radiation. Whereas, it is known that the anisotropic field in ferrites results from the presence of Fe^{2+} ions (cf. [27] p. 250), which is formed mainly during the sintering process [31] and its concentration increased by irradiation. Thus, as a summary, γ-rays irradiation decreased μ_i of all the samples due to decreasing in M and D and increasing of K. Moreover, the irradiation increases the porosity and the internal strain as reported in [18], which are considered obstacles for the domain-wall motion leading to decreasing the initial permeability.

Figure 5 presents curves of the measured values of μ_i as a function of sample temperature T (°C) for both unirradiated and irradiated samples. It was found that the curves are for typical multidomain grains showing a sudden drop in μ_i at T_C. The Curie temperature (T_C) of each investigated

Table 1 Values of magnetization, crystallite-size, and $|\Delta\mu_i/\Delta T|$ for $Mg_xCu_{0.5-x}Zn_{0.5}Fe_2O_4$ ferrite samples before and after irradiation

x	M (kA/m) at $H = 2$ (kA/m)		D (nm)		$\|\Delta\mu_i/\Delta T\|$	
	Unirradiated	Irradiated	Unirradiated	Irradiated	Unirradiated	Irradiated
0.0	8227	8190	160	144	97	73
0.2	7412	7293	155	140	114	99
0.4	5604	5152	134	92	134	125

sample is determined by drawing a tangent for the curve at the rapid decrease of μ_i. The intersection of the tangent with the T-axis determines T_C. From Fig. 5, it is observed that the rate by which μ_i decrease with temperature at T_C after irradiation was lower than that before irradiation. This could be explained as follows: the sharp decrease of μ_i with temperature at T_C reflects the homogeneity of the sample which can be expressed as $\Delta\mu_i/\Delta T$ at T_C [32, 33]. From Table 1, one can note that the values of $\Delta\mu_i/\Delta T$ for irradiated samples are lower than that of unirradiated ones, therefore, the homogeneity of irradiated samples are less than that of unirradiated ones. There are two factors leading to this result: (1) the increase of the porosity and internal strain due to irradiation. (2) The decrease of the average grain size and consequently increasing of the number of grain boundaries.

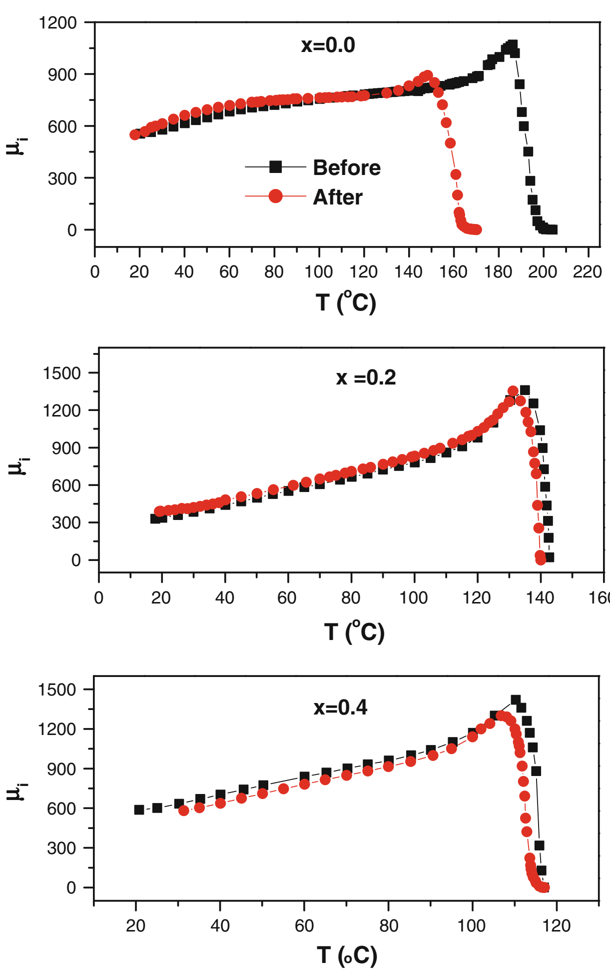

Fig. 5 Temperature dependence of initial permeability of $Mg_xCu_{0.5-x}Zn_{0.5}Fe_2O_4$ ($x = 0.0$, 0.2, and 0.4) before and after irradiation

The composition dependence of T_C for unirradiated and irradiated samples is shown in Fig. 4b. It is clear that T_C decreases with increasing Mg-concentration before and after irradiation which is in agreement with previously reported data [4, 19]. After irradiation the value of T_C was decreased for all Mg-concentrations. For the sample of $x = 0.0$, the irradiation caused a significant decrease in its Curie temperature from 195 to 165 °C. The variation of T_C with both composition and irradiation could be explained using the pair model. According to this model, the exchange energy between the magnetic moments in A and B sites, which determines the Curie temperature, decreases when the magnitude of the magnetic moments decreases and the separating distances between them increase (cf. [27], p. 147). Thus, the behavior of T_C versus Mg-concentration could be attributed to the decrease in the magnetic moments by replacing the magnetic Cu^{2+} ions by the non-magnetic Mg^{2+} ions. Also, the Curie temperature decreased due to irradiation as a result of the decrease of magnetic moments (as noticed in magnetization) and the increase of the separating distances between the moments (as indicated by lattice parameters). For the sample of $x = 0.0$, irradiation caused significant lattice distortion observed clearly by the XRDP for that sample and consequently it was of the highest decrease in T_C and μ_i values among the all samples.

Conclusion

X-ray diffractographs for the ferrite samples with chemical formula $Mg_xCu_{0.5-x}Zn_{0.5}Fe_2O_4$ (where $x = 0.0$, 0.2, and 0.4) assured the cubic spinel structure for all investigated samples with some modifications in the value of relative intensity due irradiation. Both lattice parameter and porosity of the investigated samples increased after irradiation. As a result of the irradiation process, there was disimprovement in the magnetic properties. Where, the values of magnetization, initial permeability, and Curie temperature in addition to the homogeneity were decreased by irradiation. A significant decrease in the values of μ_i (up to 54%) and T_C (up to 30 °C) for the sample with $x = 0.0$. These results reveal that the structure and the magnetic properties in the investigated system of Mg–Cu–Zn ferrites are highly affected by irradiation.

Acknowledgements The authors would like to thank the supervisor of ^{60}Co-irradiation unit, Prof. Zeinab A. Saleh, in cyclotron facility, AEA, Egypt for performing irradiation of investigated samples and calculation of the irradiation dose.

References

1. Hak PJ, Ho KJ, Hee CS (1996) Proceedings of the seventh international conference on ferrites, Bordeaux, France, vol 348, 1996
2. Qi X, Zhou J, Yue Z, Gui Z, Li L (2002) J Magn Magn Mater 251:316
3. Atassi Y, Tally M (2006) J Iran Chem Soc 3:242
4. Yue Z, Zhou J, Li L, Wang X, Gui Z (2001) Mater Sci Eng B 86:64
5. Parak J, Kim J, Cho S (1997) J Phys IV 07:C1-193
6. Ahmad MA, Bishay ST, Radwan FA (2002) J Phys Chem Solids 63:279
7. Hemeda OM, El-Saadawy M (2003) J Magn Magn Mater 256:63
8. Mazen SA, Mansour SF, Zaki HM (2003) Cryst Res Technol 38:471
9. Darwish NZ, Hemeda OM, Abd El-Ati MI (1994) Appl Radiat Isot 45(4):445
10. Fetisov VB, Kozhina GA, Fishman A Ya, Kurennykh TE, Vykhodets VB (1998) J Appl Phys 83:6876
11. Okasha N (2010) J Alloys Comps 490:307
12. Standley KJ (1972) Oxide magnetic materials, 2nd edn. Clarendon Press, Oxford
13. Poltinnikov SA, Turkevic H (1966) Sov Phys Solid State 8:1144
14. Mazen SA, Wafik AH, Mansour SF (1996) J Mater Sci 31:2661. doi:10.1007/BF00687297
15. Hemeda DM (2005) Am J Appl Sci 2:989
16. Ahmed MA, Ateia E, Abdelatif G, Salem FM (2003) Mater Chem Phys 81:63
17. Sattar AA, El-sayed HM, Agami WR (2007) J Mater Eng Perform 16(5):573
18. Bhosale DN, Choudhari ND, Sawant SR, Bakare PP (1997) J Magn Magn Mater 173:51
19. Ateia E (2006) Egypt J Solids 29(2):317
20. Hamada IM (2004) J Magn Magn Mater 271:318
21. Globus A, Duplex P, Guyot M (1971) IEEE Trans Magn 7:617
22. Globus A, Duplex P (1968) J Appl Phys 39:727
23. Baca G, Valenzuela R, Escobar MA, Magña LF (1985) J Appl Phys 57:4183
24. Globus A, Guyot M (1972) Phys Status Solidi B 52:427
25. Murthy VRK, Raman R, Viswanathan B (1989) Proceedings of the fifth international conference on ferrites, Bombay, January, 1989, vol 447. Oxford and IBH, New Delhi
26. Rezlescu N, Rezlescu E, Popa PD, Craus ML, Rezlescu L (1998) J Magn Magn Mater 182:199
27. Chikazumi S, Charap SH (1964) Physics of magnetism, vol 91. Wiley, New York
28. Bhosale DN, Sawant SR, Gopalkrishnan GV, Chougule RS (1998) J Mater Sci 9:331. doi:10.1023/A:1008972918402
29. Rado GT, Folen VJ, Emerson WH (1956) Proc IEEE 104:198
30. Okamura T, Kojima Y (1952) Phys Rev 86:1040
31. Gorter EW (1954) Philips Res Rep 9:295
32. Cedillo E, Ocampo J, Rivera V, Valenzuela R (1980) J Phys E 13:383
33. Sattar AA, Samy AM (2002) J Mater Sci 37:4499