Improvement of sintering and magnetic properties of nanocrystalline Mn-Zn ferrites

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Abstract: The effect of sintering temperature on the formation of Mn-Zn ferrites in a single phase cubic spinel structure has been investigated. Samples of general chemical formula Mn1-xZnxFe2O4, (0.0 ≤ x ≤ 0.5) were prepared using standard ceramic technique. The obtained results show that 1300oC for 15h with heating rate 2oC/min are suitable conditions for the preparation of Mn-Zn ferrites. The effect of the double final sintering and Zn2+ ions concentration on the physical properties of Mn-Zn ferrite was also investigated. XRD data confirm the formation of the samples in single phase cubic spinel structure. The crystallite size (t) of samples was estimated by Scherrer's formula and found in the range (90-115 nm). Energy dispersion X-ray analysis (EDX) was used for the elemental analysis of the prepared samples. Magnetization of the samples was measured using Faraday's method as a function of temperature at magnetic field 1300Oe. The Curie temperature of the prepared samples was found to be decreases with increasing Zn2+ion. The hysteresis parameters such saturation magnetization Ms and coercivity Hc of the prepared samples were measured at room using vibrating sample magnetometer (VSM). An improvement in the physical properties of Mn-Zn ferrite was observed due to the preparation conditions compared with the published data.

Keywords: Mn-Zn Ferrites, Sintering, EDX, VSM; Curie temperature; Magnetization, Hysteresis Parameters.

1. Introduction

Ferrites are ceramic materials of high magnetic properties and they are mainly used as a core for inductors, transformers and recording heads [1-3]. The resistivity of Mn-Zn ferrite is relatively small with high eddy current loss, so many methods of preparation was used to improve its physical properties. Mn-Zn ferrites have been studied by many authors with different preparation methods such as chemical co-precipitation method by E.Veena et.al [4], hydrothermal precipitation processing by Y.Xuan et. al [5] and reverse micelle technique by P. Poddor et.al [6]. Also D. Ravinder et. al studied the dc electrical resistivity of Mn-Zn ferrite as function of temperature [7].

It is well known that, the cation distribution and consequently the physical properties of the ferrites depends on the preparation conditions such as the sintering temperatures and the cooling rate [8]. In our previous work we study the effect of heating rate on the electrical properties of Mn-Zn ferrites and the obtained results shown that, the heating rate controlled all the electrical characteristics of the samples due to the change in the grain size [9]. The saturation magnetization of the Mn-Zn ferrites depends on the solubility of the cations $Mn^{2+}$and Zn^{2+} ions in the ferrite lattice and the occupying positions of tetrahedral or octahedral sites [10]. So, the preparation method and the preparation conditions are very important to control the magnetic properties of Mn-Zn ferrites.

In present work we study the effect of sintering temperature on the formation of Mn-Zn ferrites in a single phase cubic spinel structure. Moreover, the present work investigates the effect of double sintering and Zn^{2+} ions concentration (x) on the magnetic properties of Mn-Zn ferrites.

2. Experimental Techniques

Ferrites with general chemical formula $Mn_{1-x}Zn_xFe_2O_4$, ($0.0 \le x \le 0.5$ step 0.1) were prepared

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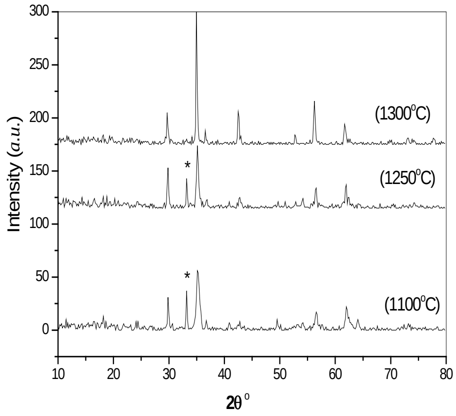
using the standard ceramic technique. High purity oxides in stoichiometric ratio were used and well grinded for 4 h and pre-sintered in air at 900°C for 5h with heating rate 4 °C/min using furnace then slow cooled to room temperature. After that, the samples were ggrinded again for 3 h and the mixture was pressed into pellets using uni-axial press of pressure $1.9x10^8$ Nm^{-2}. The sample of $Mn_{0.9}Zn_{0.1}Fe_2O_4$ was final sintered in air in a closed oven at three different temperatures 1100°C, 1250°C and 1300 °C for 15h to study the effect of sintering temperature on the formation of single phase Mn-Zn ferrites. The final sintering of all the samples was carried out in two steps at 1100 °C for 10h then at 1300 °C for 15h with a heating rate 2°C/min. Crystalline phases in of the different samples were identified using XRD on a Brucker axis D8 diffractometer using Cu-K_{α}. The elemental analysis was performed using energy dispersive X-ray (EDX). The magnetization of the investigated samples was measured using Faraday's method. Also, the hysteresis loop parameters were measured using the vibrating sample magnetometer (VSM) of a magnetizing field ranged from 0 to 6000 Oe.

3. Results and Discussion

3.1. Structural properties

Crystal structure of all the prepared samples was examined using XRD patterns. The XRD patterns of the prepared samples at different sintering temperatures 1100, 1250 and 1300 °C are shown in Fig.1. Figure 1 shows that, the samples prepared at 1100 and 1250 °C exhibit a peak of Fe_2O_3 secondary phase but the prepared sample at 1300 °C has a single phase cubic spinel structure. The obtained results investigate that, the final sintering temperature at 1300 °C for 15h with heating rate 2 °C/min are suitable conditions for the preparation of single Mn-Zn ferrites. Fig. 2 shows the XRD patterns of all the prepared ferrite samples. The figure indicates that the samples are have a single phase cubic spinel structure where the crystallographic planes of the characteristic peaks of cubic spinel structure are perfectly matched with the theoretical data of Franklinite spinel structure (ICDD card No. 74-2402).



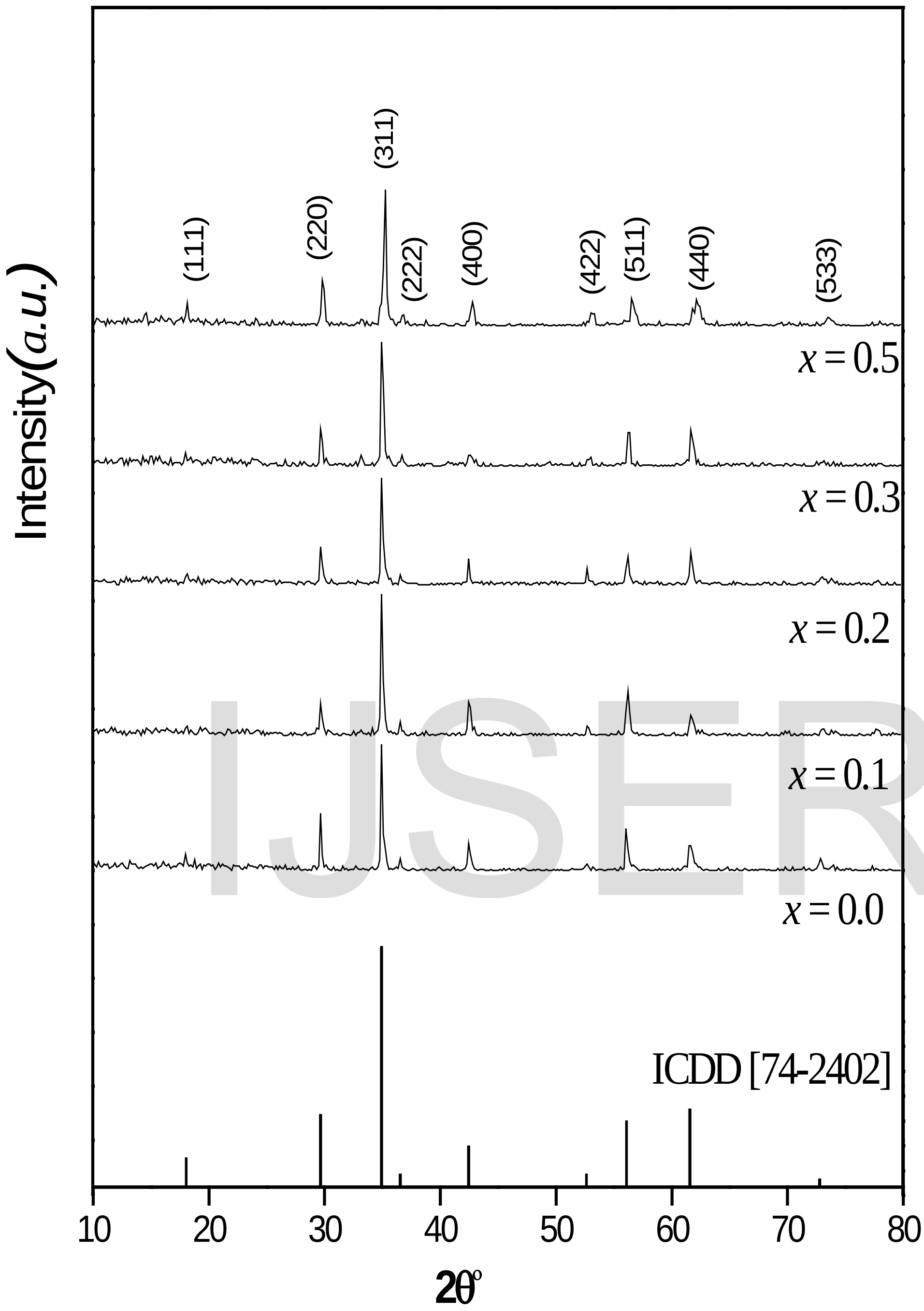


Fig. 2: X-ray diffraction patterns of all the samples $Mn_{1-x}Zn_xFe_2O_4$

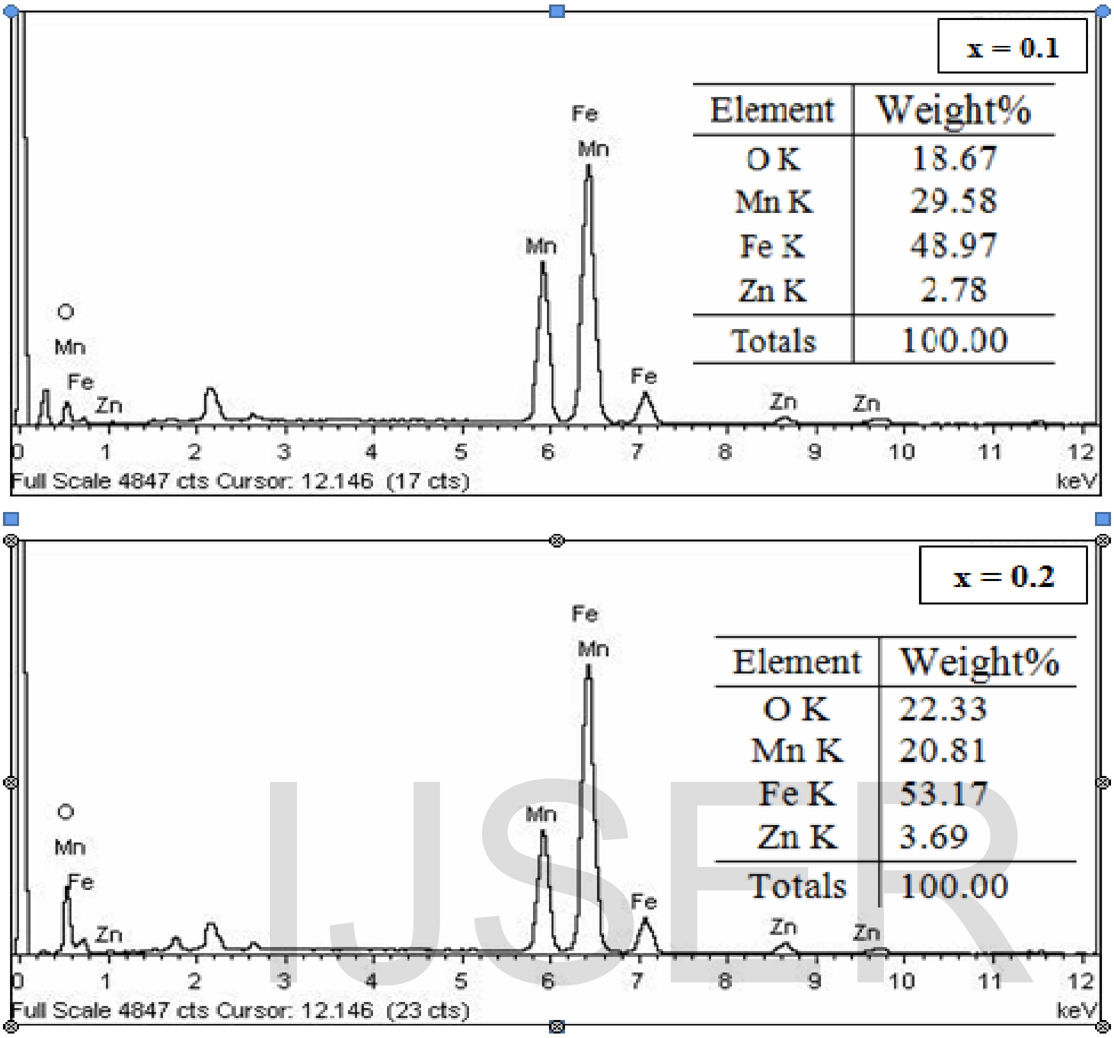


Fig. 3: EDX data for the samples of x = 0.1 and x = 0.2.

The crystallite size (t) of the prepared samples was estimated using Scherrer's equation [11] and the calculated crystallite size (t) as a function of Zn content (x) shows that, the substitution of Mn^{2+} ions by Zn^{2+} ions results in a decrease in the crystallite size from 115 nm to 90 nm. Compositional analysis using energy-dispersive X-ray spectroscopy (EDX) was carried out on these compositions and the obtained results are shown in shown in Fig. 3. The ratios as determined by EDX measurements for x = 0.1 and x = 0.2 are compared with the prepared ratios as shown in Table [1]. Table [1] shows that, the stoichiometric values are very close to the measured values.

Table 1: EDX measurements for samples x = 0.1 and x = 0.2**.**

Sample	ratio	Prepared ratio	Average EDX ratio
$Mn_{0.9}Zn_{0.1}Fe_2O_4$	Mn:Fe	0.45	0.5
	Zn:Fe	0.05	0.056
$Mn_{0.8}Zn_{0.2}Fe_2O_4$	Mn:Fe	0.4	0.39
	Zn:Fe	0.1	0.11

3.2. Magnetic properties

3.2.1. Magnetization

The magnetization (M) of the prepared samples was measured as a function of temperature and the obtained results are shown in Fig. 4. Also the temperature dependence of the Magnetization for all studied samples at 1300 Oe is shown in Fig. 5. Figures 4, 5 show a normal ferrimagnetic character as the general trend for all the spinel ferrites where the magnetization of the prepared samples decreases gradually with increasing the temperature until the Curie temperature T_C after which the sample shows a paramagnetic trend [12, 13].

Figure 6 shows the compositional dependence of the magnetization at room temperature. This figure shows that, as Zn-content increases M increases up to $x = 0.1$ and then decreases. The increase in the magnetization with increasing Zn-content is attributed to Zn^{2+} ions of zero magnetic moment should occupy the A-site instead of Mn^{2+} ions of magnetic moment $5.85\mu_B$, then the magnetization of A-site decreases. According to the Neel`s two sublattice collinear model, the net magnetization ($M = M_B - M_A$) increases and the maximum magnetization was obtained at $x = 0.1$. But with more increase of Zn-content M decreases, by assuming a combination of parallel and anti-parallel moments, since Zn-ferrite is known to be paramagnetic, it is expected that the B-B interaction will be antiferromagnetic even in the mixed Zn ferrite. The effect of this interaction is usually masked by strong A-B interaction which causes the spins in B-site to be aligned parallel to each other. If, however, the A-B interaction is weakened by introducing non-magnetic Zn^{2+} ions into A-site then the tendency toward an anti-ferromagnetic arrangement in the B-site will be increased [14]. For high Zn^{2+} concentration Yafet-Kittel model is obeyed in which the nonlinearity in the B-site is reflected by Y-K angle between the moments in the B-site which is responsible for the deviation from the Neel`s collinear model. So for $x \geq 0.2$, the magnetization decreases due to the increases in the Y-K angle ($M = M_B \cos\theta_{YK} - M_A$) [15, 16].

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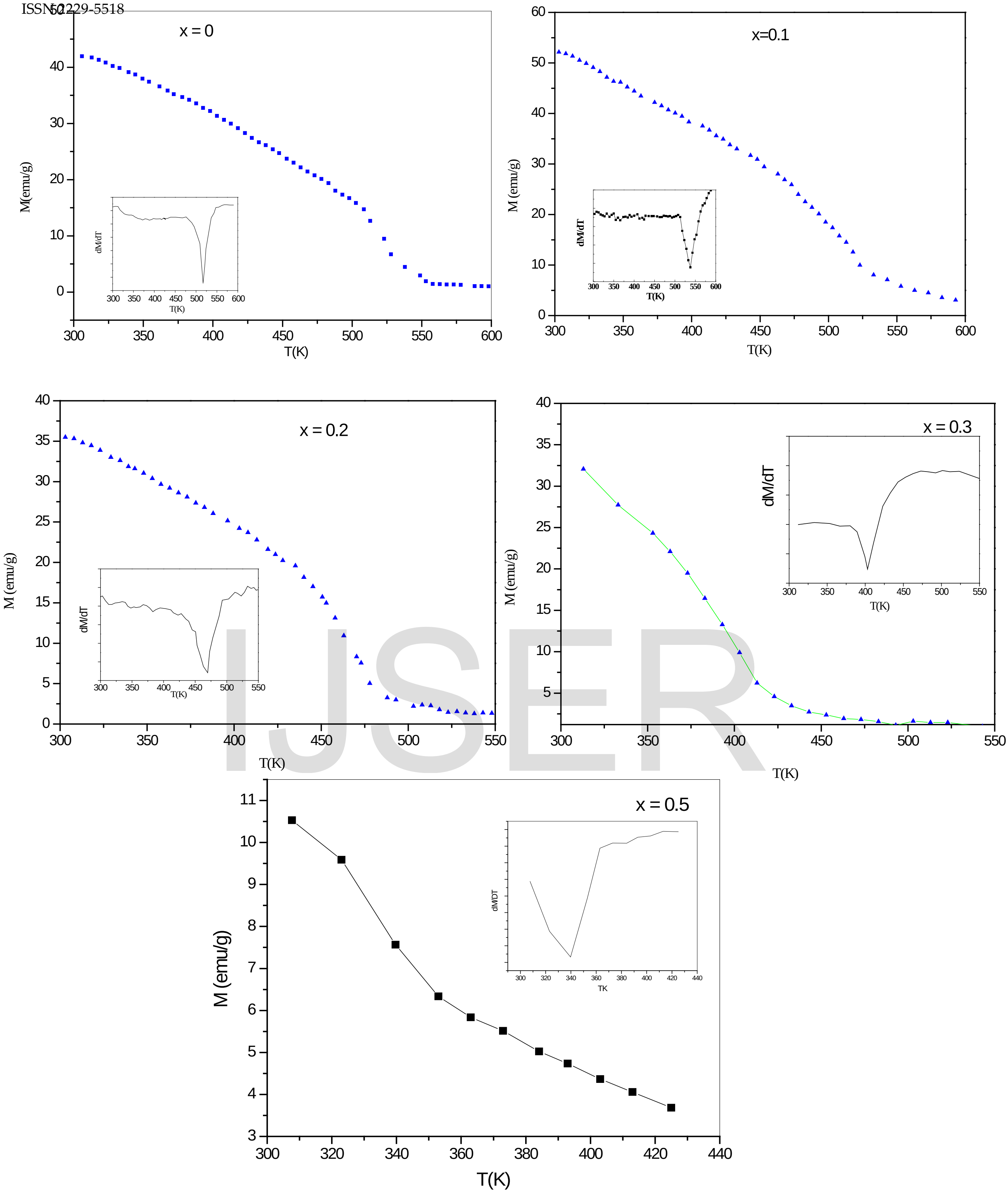

Fig. 4: The variation of the magnetization and the onset $\frac{dM}{dT}$ as a function of absolute temperature T(K) at a magnetic field 1300Oe for $Mn_{1-x}Zn_xFe_2O_4$ system; $(0.0 \leq x \leq 0.5)$.

The Curie temperature of the prepared samples was determined by plotting the first derivative of the magnetization $\frac{dM}{dT}$ as a function of absolute

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temperature, as an inset in Fig.4. The compositional dependence of the Curie temperature (T_C) is shown in Fig. 6. The figure shows that, the Curie temperature (T_C) decreases with increasing Zn content (x). The decrease in the Curie temperature is due to the substitution of Mn^{2+} ions by non-magnetic Zn^{2+} ions at tetrahedral A-site. The substitution of nonmagnetic Zn^{2+} ions reduces the active magnetic linkages per magnetic ion per formula unit; as a result (T_C) decreases with increasing Zn-content [17]. In other wards the increase in the non-magnetic Zinc ions reduces the magnetic moment of the A- sub-lattice as the Zn^{2+} ions preferentially occupy the A- sites of the spinel lattice thereby reducing the A-B exchange interaction between A and B sub-lattices, this results in a reduction in the Curie temperature [18].

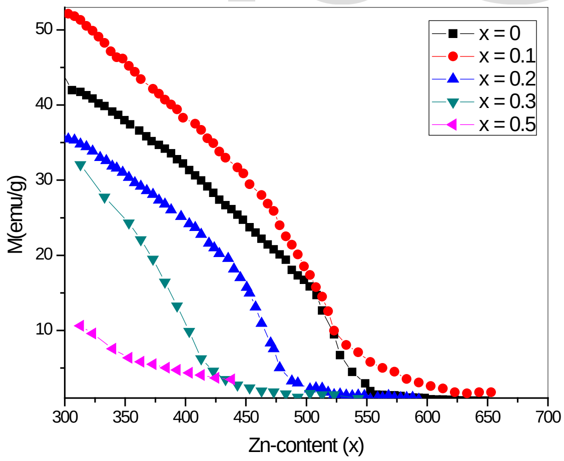

Fig. 5: Magnetization vs the absolute temperature T(K) for the samples $Mn_{1-x}Zn_xFe_2O_4$; ($0.0 \le x \le 0.5$) at 1300 Oe.

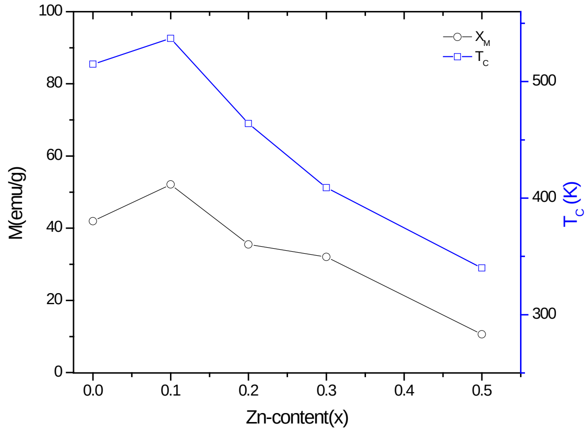

Fig. 6: variation of the Magnetization (M) and Curie temperature vs Zn^{2+} content (x) at room temperature.

3.2.2. Vibrating sample magnetometer

The hysteresis parameters of the prepared samples were measured at room temperature and the hysteresis curves are shown in Fig. 7. The figure shows a hysteresis in the samples indicating a ferromagnetic behavior where the magnetization increases with increasing the applied magnetic field and attains its saturation value at higher field. The effect of the substitution by Zn^{2+} ions on the magnetization M_s, remanence M_r and coercivity H_c of the prepared samples at room temperature and maximum field of 6000 Oe are summarized in Table [2]. The small values of the remanence magnetization confirm the soft character of the samples. The obtained results show that, as Zn content increases the saturation magnetization decreases, this is expected on basis of the substitution of Mn^{+2} ions by nonmagnetic Zn^{2+}ions.

The high values of the coercivity H_c of the prepared samples means that the samples have high resistance to be demagnetized which is useful in the magnetic applications.

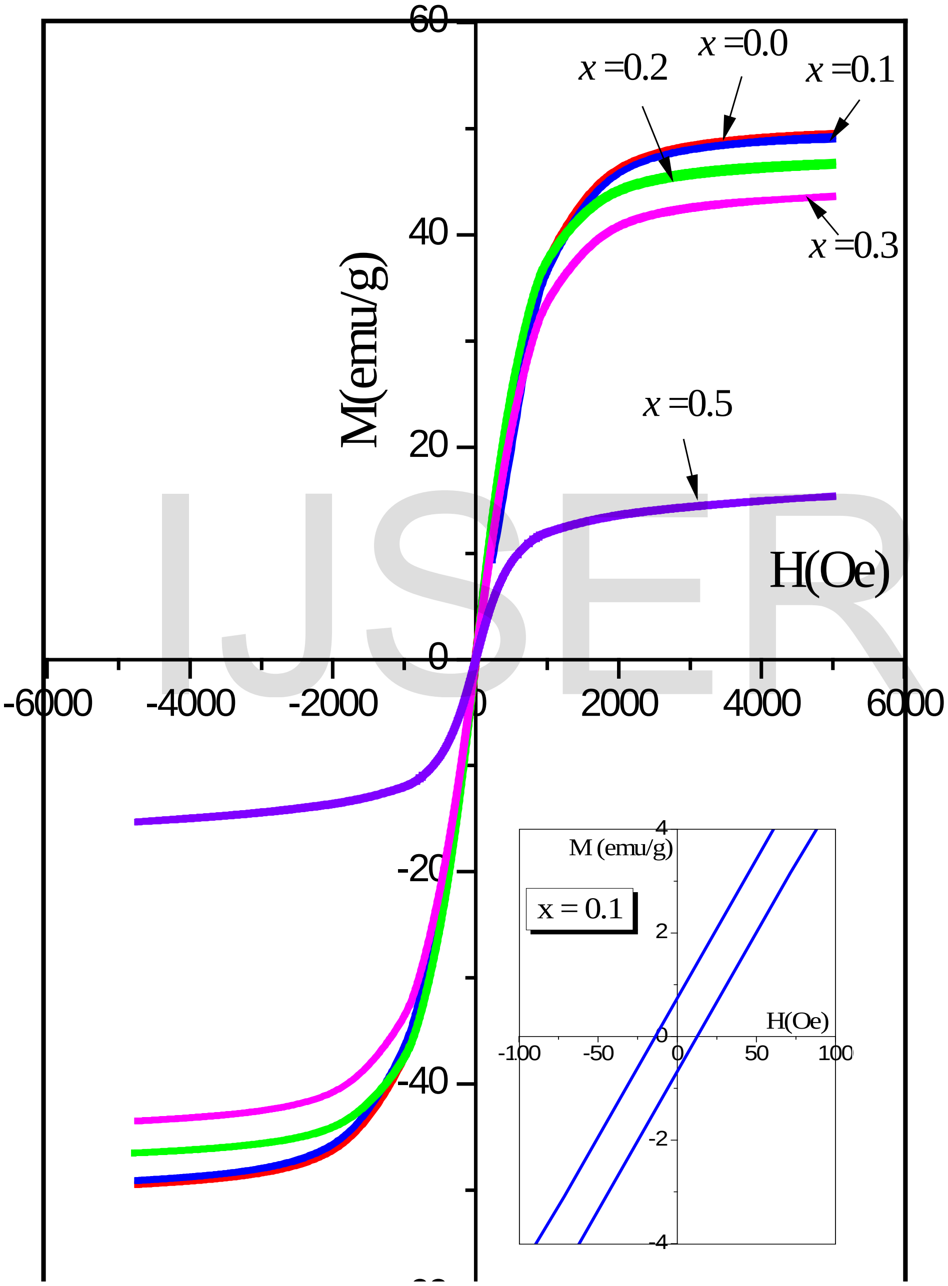

Fig. 7: The DC hysteresis curves for the prepared samples $Mn_{1-x}Zn_xFe_2O_4$

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Comparison with the previous work

The obtained results show that, the final sintering of the samples in two steps relatively improves some of the physical properties of

Mn-Zn ferrites compared with the published ones. The obtained results for $Mn_{0.9}Zn_{0.1}Fe_2O_4$ are summarized in Table [3] and compared with some of the published data.

Table 2: Effect of Zn^{2+} ions substitution on the magnetization M_S, remanence M_r and coercivity H_c

x	M_s (emu/g)	M_r (emu/g)	H_c (Oe)
0.0	49.2	0.70	13.2
0.1	49.5	0.94	16.6
0.2	46.7	0.63	10.4
0.3	43.5	0.60	11.6
0.5	15.4	0.42	15.6

Table 3: The obtained data compared with the published data for $Mn_{0.9}Zn_{0.1}Fe_2O_4$.

work	Crystallite size (nm)	Preparation methods	Saturation magnetization M_s (emu/g)	Hc(Oe)	Curie temperature T(K)
Present work	108	stander ceramic technique	49.5	16.6	537
Hessien et. al [13]	125	solid-state reaction	37.36	6.186	-----
Veena et. al [4]	18.9	chemical co-precipitation techniques	56	14	783
Arulmurugan el. al [10]	11.3	chemical co-precipitation techniques	42.4	12.8	633

4. Conclusions

1- Sintering conditions of 1300ºC for 15h with heating rate 2ºC/min is suitable conditions to obtain Mn-Zn ferrites in single phase cubic spinel structure.

2- XRD measurements confirm the formation of the prepared samples in single phase cubic spinel structure with crystallite size ranged from 90 to 115 nm.

3- Lattice parameter and crystallite size (t) of the prepared samples were decreases with increasing Zn^{2+} content.

4- EDX measurements show that, the stoichiometric values are very close to the measured values.

5- Magnetization was increased up to $x = 0.1$ and then decreased with increasing Zn^{2+} content.

6- The Curie temperature of the samples was decreases with increasing Zn^{2+} content.

7- VSM was investigated at room temperature and shows a hysteresis indicating a ferromagnetic behavior and an improvement in the magnetic properties was observed.

8- The obtained results shows that the final sintering of the samples in two steps improves some of the physical properties of Mn-Zn ferrites compared with the published ones.

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References

[1] K. Ishino, Y. Narumiya, Development of magnetic ferrites: control and application of losses", Ceram Bull. Vol 66, pp 1469, 1987.

[2] A. Goldman, Modern Ferrite Technology 2nd ed.USA, 2006

[3] U. Ghazanfar, S.A. Siddiqi, G. Abbas, Structural analysis of the Mn-Zn Ferrite, using XRD technique, Mater. Sci. Eng. B, Vol 118, PP 84, 2005.

[4] E.Veena Gopalan, I.A.Al-Omari, K.A.Malini, P.A.Joy, D.SakthiKumar, Y.Yoshida, M.R.Anantharaman, Impact of zinc substitution on the structural and magnetic properties of chemically derived nanosized manganese zinc mixed ferrites, J. Magn. Magn. Mat.,Vol 321, pp 1092,2009.

[5] Yimin Xuan, Qiang Li, Gang Yang, Synthesis and magnetic properties of Mn-Zn ferrite nanoparticles, J . Magn. Magn. Mat.,Vol 312, pp 464, 2007.

[6] P. Poddar, H. Srikanth, S.A. Morrison, E.E. Carpenter, Inter-particle interactions and magnetism in manganese-zinc ferrite nanoparticles J. Magn. Magn. Mat., Vol 288, pp 443, 2005.

[7] D. Ravinder and K. Latha , Electrical conductivity of Mn–Zn ferrites, J Applied physics, Vol 75, pp 6118, 1994.

[8] T. A. S. Ferreira, J. C. Waerenborgh, M. H. R. M. Mendonc , M. R. Nunes and F. M. Costa, structural and morphological characterization of $FeCo_2O_4$ and $CoFe_2O_4$ spinels prepared by a coprecipitation method, Solid State Sci., Vol 5, pp 383,2003.

[9] M. A. Ahmed, K. A. Darwish, E. H. EL-Khawas, Heating rate effect on the electrical properties of $Mn_xZn_{1-x}Fe_2O_4$ ferrite (x = 0.28, 0.48, 0.64 and 0.76), J. Mat.Sci Letters, Vol 16, pp 1948,1996.

[10] R. Arulmurugan, B. Jeyadevan, G. Vaidyanathan, S. Sendhilnathan, Effect of zinc substitution on Co-Zn and Mn-Zn ferrite nanoparticles prepared by coprecipitation, J. Magn. Magn. Mat. Vol 288, pp 470, 2005.

[11] W.D. Kigery, H.K. Bowen, D.R. Uhlmann, Introduction of Ceramics, John Wiley& Sons. NewYork; pp 458, 1975.

[12] S. Unnikrishnan, DK Chakrabarty, Magnetic properties and domain state of the magnesium ferrite-magnesium titanate solid solutions, Phys. Stat. Sol. A, Vol 121, pp 265, 1990.

[13] M.A. Ahmed, N. Okasha, M. Gabal, Electrical transport properties of barium-titanium ferrite

ISSN 2229-5518
with a hollandite structure, Mat.Chem. Phys., Vol 99, pp197, 2006.

[14] S. ChikaZumi, S. Charap, Physics of Magnetism, New York, London, Sydney,1964.

[15] S.V. Kshirsagar, V.N. Dhage, S.J. Shukla, K.M. Jadhav, Influence of Mn-Zn Co-substitution on the structural and magnetic properties of magnesium ferrite, Inter. J Eng. and Adv. Techn., Vol 2(5), pp 2249, 2013.

[16] A.A. Sattar, H.M. El-Sayed, K.M. El-Shokrofy, M.M. El-Tabey, Improvement of the magnetic properties of Mn-Ni-Zn ferrite by the non magnetic Al-ion substitution, J. of Applied Sciences, Vol 5 (1), pp162,2005.

[17] D.S. Birajdar, D.R. Mane, S.S. More, V.B. Kawade, K.M. Jadhav, Structural and magnetic properties of $Zn_xCu_{1.4-x}Mn_{0.4}Fe_{1.2}O_4$ ferrites, Materials Letters, Vol 59, pp 2981, 2005.

[18] M.M. Hessien, M.M. Rashad, K. El-Barawy, I.A. Ibrahim, Influence of manganese substitution and annealing temperature on the formation, microstructure and magnetic properties of Mn-Zn ferrites, J. Magn. Magn. Mate., Vol 320, pp 1615, 2008.