

Superparamagnetic Behaviour Of Mn Substituted Zn Ferrite Nanoparticles for RF Application

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Abstract: Manganese substituted zinc ferrite nanoparticles ($Mn_x Zn_{1-x} Fe_2O_4$ with $x = 0, 0.5, 1$) were synthesized via sol-gel auto combustion route. X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and electron dispersive X-ray (EDX) have been used to investigate the prepared Magnetic Zinc Nano crystal (MZN). Magnetic properties of the prepared samples have been detected by vibrating sample magnetometer (VSM), at room temperature and the results of the prepared MZN exhibits a superparamagnetic (SPM) behaviour. SPM nanocrystals are promising applications in medical science such as drug delivery, bioseparation and magnetic resonance imaging (MRI).

Keyword: Magnetic measurements, Superparamagnetism.

I. INTRODUCTION

Spinel ferrites are most widely used magnetic material due to the low cost. Mn-Zn ferrites have many important applications, particularly in electronics and engineering industry [19]. However, ($Mn_x Zn_{1-x} Fe_2O_4$ with $x = 0.5, 1$) exhibits superparamagnetic (SPM) behavior by using the study of VSM. Superparamagnetism is a form of magnetism, which appears in small ferromagnetic or ferrimagnetic nanoparticles. In nanoparticles, magnetization can randomly flip direction under the influence of temperature. Typical time between two flips is called "Neel relaxation time". In the absence of external magnetic field, the time used to measure the magnetization of the nanoparticles is much longer than the "Neel relaxation time". Their magnetization appears to be in an average zero. They are said to be in the Superparamagnetic state. An external magnetic field is able to magnetize the nanoparticles. In paramagnetism, their magnetic susceptibility is large.

SPM is not just an abstract topic of study in advance physics. But it also has a practical applications in the medical field such as MRI technology, DNA & RNA experimentation treatment of hyperthermia and drug delivery [1-10]. It is also used in high-tech sensors (of the sort used in aerospace technology) and other aspect of nanotechnology. For high performance applications in biomedicine, the magnetic nanocrystals are required to possess small width in proportion to length distribution and uniform spherical shape that gives superparamagnetic properties [11, 12]

II. EXPERIMENTAL

2.1 Preparation of sample:

Powder of MZN ferrites particles were prepared by sol-gel auto combustion method. by Using analytical grade chemical reagents of $Mn(NO_3)_2 \cdot 4H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and $Fe(NO_3)_3 \cdot 9H_2O$ and its stoichiometric proportions were first dissolved in deionized water. The mixture of solution was heated at 800c till the complete mixture transformed in to gel. The gel of the solution which were ignited and burnt by microwave oven on 600 watt for 7 minute to obtain ash powder. The powders were annealed slowly at 8000c in a furnace for 4 hours after intermediate grinding.

2.2 Characterization Technique:

The phase identification and crystalline structural analysis of the thermally treated powder was analyzed by X-ray diffraction (XRD, Bruker AXS D8 advance, Cu $K\alpha$ radiation $\lambda = 0.1540$ nm). The size and morphology of such prepared samples were characterized by scanning electron microscopy. (SEM, Camca SU, SEM probe) and transmission electron microscopy (TEM, Phillips, CM-200) for magnetic hysteresis loops were measured using a vibrating sample magnetometer (VSM. Lakeshore 7410)

III. RESULTS AND DISCUSSION

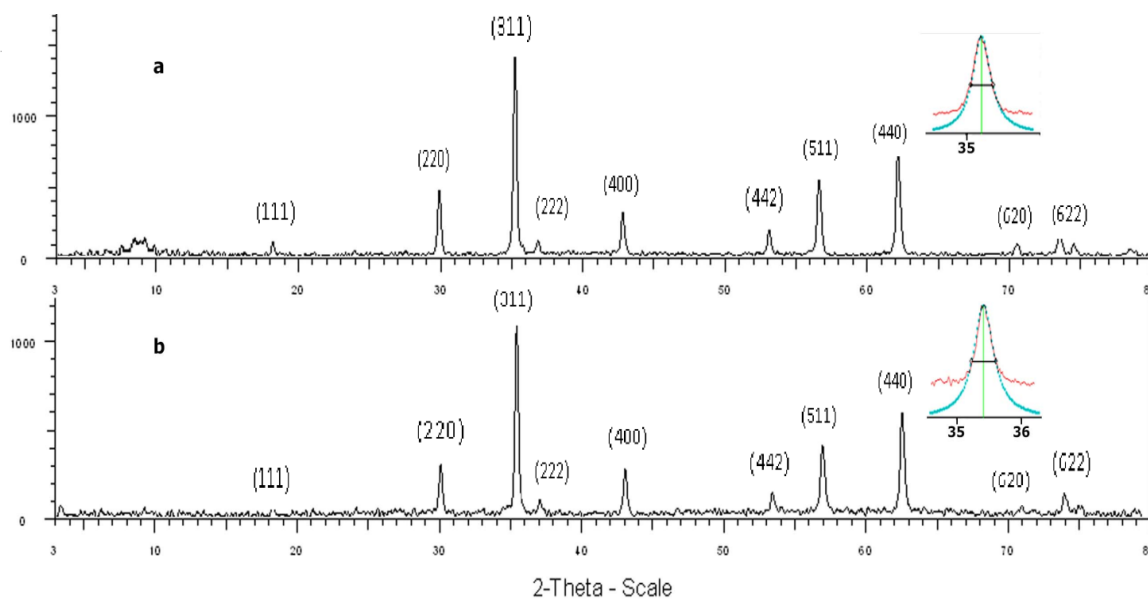


Fig.1. a & b) shows XRD pattern and broadening of high intensity peak

The crystalline structures of MZN were characterized by XRD as shown in above fig.1 (a) & (b). All the Bragg's reflections have been indexed which confirmed the formation of simple cubic spinel structure in single phase without any impurity peak. The strongest reflection and broadening of high intensity peak comes from the (311) planes as depicted by JCPDS card 74-2403, which denote the spinel phase appearing at 35.070 & 35.110. The crystalline size were calculated for $(\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4)$ with $x = 0.5, 1$ using high intensity (311) peaks and using Scherer formula i.e. $dhkl = 0.9 \lambda / \beta \cos\theta$. The values are found to be 15nm and 16 nm. The lattice parameter for $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and MnFe_2O_4 The values are found to be 8.4812 Å & 8.4699 Å. It was found that the lattice parameter decreases with increasing cations substitution of Mn^{2+} due to difference of ionic radius (ionic radius of Zn^{2+} is 1.35 Å & Mn^{2+} is 1.40Å) and its atomic mass.

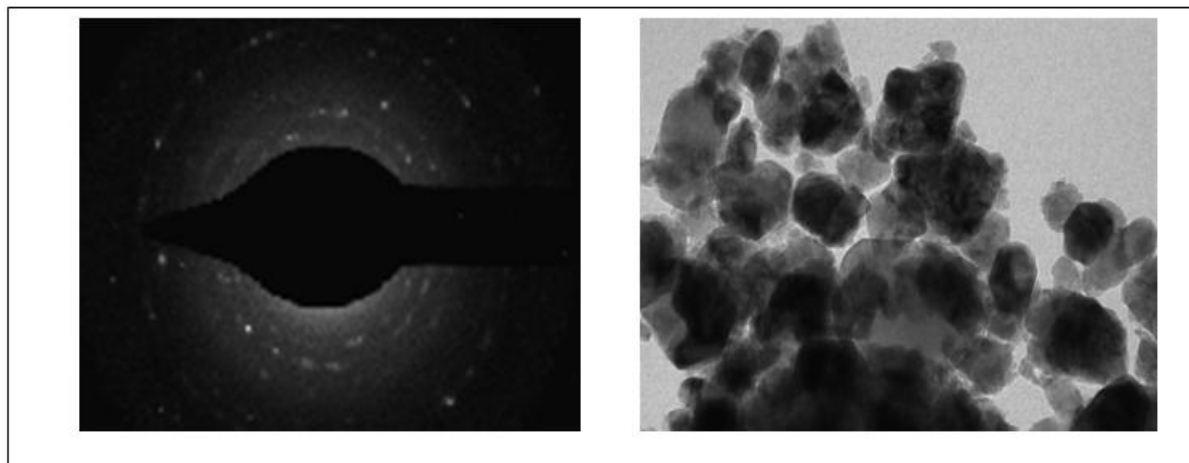


Fig .2 A typical TEM image of $\text{Mn}_x\text{Zn}_x\text{Fe}_2\text{O}_4$, $x=0.5, 1$ nanoparticles.

A typical TEM image of the prepared MZN nanocrystals has been shown in above fig.2. The circular diffraction rings are clearly visible, indicating the nano-crystalline nature of MZN. Most of the such prepared magnetic nanocrystals are nearly spherical structure as per shown in TEM. Dark regions are representative nanoparticles which are in agreement with the SEM findings below.

The morphological studies of the Mn-Zn ferrite powder was carried out using SEM. This type of electron microscope is capable of producing high resolution images of a sample surface [13-14] due to the manner in which the images are created. SEM images have a characteristic three dimensional appearance and are useful for judging the surface structure of Mn-Zn ferrite. It is found that the powders were made up of

particles with the size in the nano range as shown in fig.3. In which the powder form of the solid sample was mounted on the conducting resin with dispersion treatment, indicating that the almost spherical and homogeneous nanoparticles with the average size of MZN are about 28 nm. This result is in agreement with the result of XRD and TEM analysis [17].

The chemical composition of such prepared ferrites samples was further confirmed by energy-dispersive X-ray analysis (EDX). The result shows that Me^{2+}/Fe^{3+} ratio is about 0.5 which is in agreement with the expected stoichiometry in each case as shown in fig.3 EDX system are attachment to SEM or TEM instrument where the imaging capability of the microscope identifies the specimen of interest. The data generated by EDX analysis consist of spectra showing peak of Mn, Fe, and O, corresponding to the elements making up the true composition of the sample being analysed. The EDX technique is non-destructive and specimen of interest can be examined in situation with little or no sample preparation.

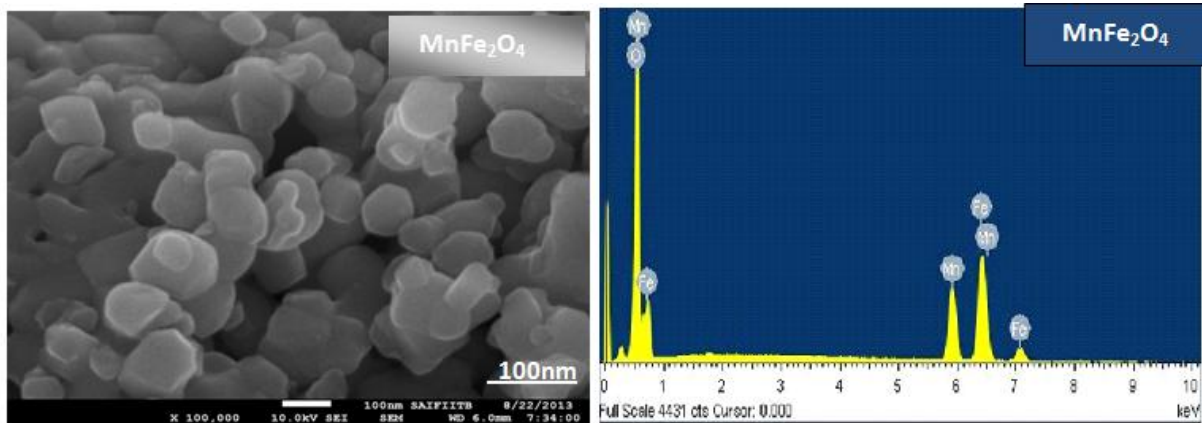


Fig 3.SEM and EDX spectrum of the sample Mn Fe₂O₄

The magnetic properties of the prepared MZN were investigated with a VSM as shown in Fig.4.

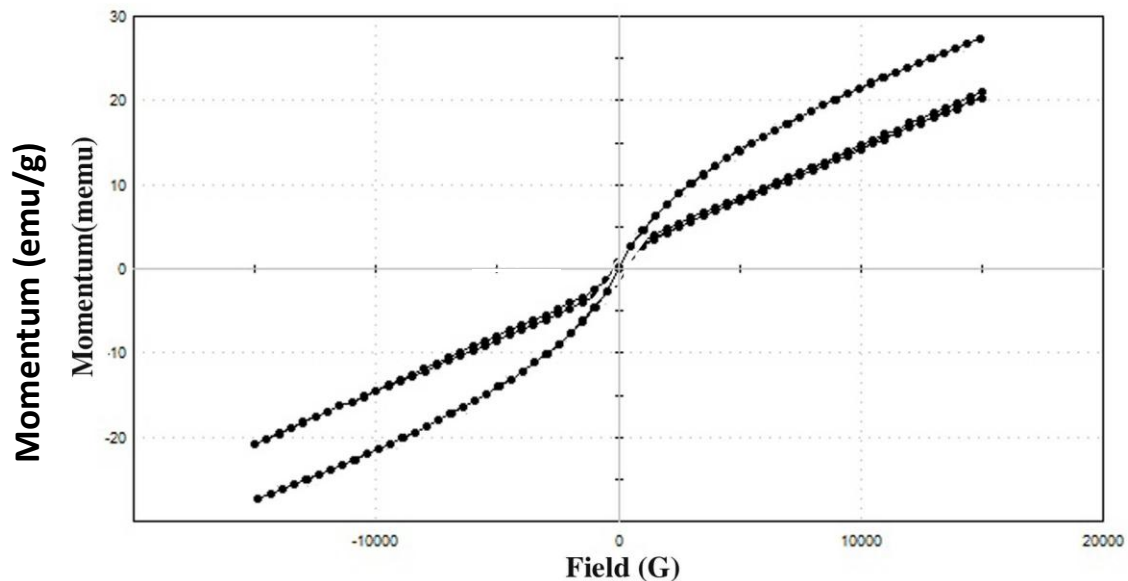


Fig 4: Magnetisation curve of nanocrystalline Mn_XZn_{1-X}Fe₂O₄ with X = 0.5,1. At room temp.

The magnetization curves measured at room temperature, from the curve the measured magnetic saturation values are about 28 emu/g for Mn_{0.5}Zn_{0.5}Fe₂O₄ and 20 emu/g for MnFe₂O₄. The corecivity of the as prepared magnetic nanocrystals at room temperature is negligible, because in a nano size particals many single domains are uniformly magnetized with all the spins aligned in the same direction. The magnetization will be in reversed spin rotation, since there are no domain walls to move. I.e. this is the reason for the very high coercivity observed in thin research module with reported values between 38 between 177 Gauss in small nano particles [18, 20]. The superparamagnetic behaviour can be represented by hysteresis curve as shown in fig.4. Superparamagnetism occurs in nanoferrites which are single domains i.e. composed of a single magnetic

domain. This is possible only when their diameter measures below 3-50 nm, depending on the materials. Superparamagnetic materials do not retain any significant amount of magnetization in the absence of externally applied magnetic field and thus do not form aggregates.

A curve between magnetization and applied field (20kG) at room temperature is shown in fig.4. It shows typical superparamagnetic nature with no trace of hysteresis and coercivity 38G and almost zero remanence. It also prominently showed non-attainment of saturation magnetization even at 20KG.

The nonsaturation of M-H loop and the absence of hysteresis remanence and coercivity at room temperature strongly suggests the presence of superparamagnetic behavior. The values of M_s are higher in multidomain bulk ferrites (45 emu/g) [15], than the Mn-Zn compounds represented in the present work ($M_s=28$ emu/g).

The lower values of saturation magnetization and nanocrystalline ferrites pertaining to the fact that the surface effect play vital role in supporting noncollinearity of magnetic moments on their surface. Nanocrystalline particles consist of ferromagnetically aligned core spins and spin-glass like surface layers. The disordered behavior in spin from the surface of the nanoparticles pushes to modify the magnetic properties of these materials specially when surface/volume ratio is very large [16].

IV. CONCLUSIONS

We have successfully synthesized single phase simple cubic spinal polycrystalline of MZN ferrite and particles with an average crystalline size of 28 nm by sol-gel route.

We observed from the XRD, that the lattice parameter decreases with increasing cation substitution. The prepared MZN ferrites exhibits' superparamagnetic behavior at room temperature. The Superparamagnetic properties of MZN ferrites are significant for biomedical applications. Such as drug delivery, bioseparation and magnetic resonance imaging. From our research and findings, it seems that the sol-gel auto combustion method may offer to synthesis other ferrite nanocrystals with novel magnetic properties.

REFERENCES

- [1]. F. Li, H. Wang, J. Magn. Mater. 309 (2007) 295.
- [2]. S. Y. Zhao, R. Qiao, X.L. Zhang, Y. S. Kang, J Phys. Chem. C111 (2007) 7875.
- [3]. S. Sun, H. Zeng, D. B. Robinson, S. Raoux, P. M. Rice, S.X. Wang, G. Li, J. Am. Chem. Soc. 126 (2004) 273.
- [4]. H. Deng, X. Li, Q. Peng, X. Wang, J. Chen, Y. Li, Angew. Chem. Int. Ed. 44 (2005) 2782.
- [5]. T. Hyeon, Y. Chung, J. Park, S. S. Lee, Y. W. Kim, B. H. Park, J. Phys. Chem. B 106 (2002) 6831.
- [6]. S. R. Ahmed, P. Kofinas, Macromolecules 35 (2002) 3338.
- [7]. L. Li, G. Li, R. L. Smith H. Inomata, Chem. Mater. 12 (2000) 3705.
- [8]. V. Berbenni, C. Milanese, G. Bruni, A. Marini, I. Pallecchi, Thermochim. Acta 447 (2006) 184.
- [9]. H. Yang, X. Zhang, C. Huang, W. Yang, G. Qiu, J. Phys. Chem. Solids 65 (2004) 1329.
- [10]. T. Meron, Y. Rosenberg, Y. Lereach, G. Markovich, J. Magn. Mater. 292 (2005) 11.
- [11]. J. Park, J. joo, S.G. Kwoon, Y. Jang, T. Hyeon, Angew. Chem. Int. Ed. 46 (2007) 4635.
- [12]. D. Caruntu, B.L. Cushing, G. Caruntu, C.J.O'Connor, Chem. Mater. 17 (2005) 3398.
- [13]. P.I. Slick, in Ferromagnetic materials, E.P. Wohlearth, Ed, Vol.2, 196, North-Holland, Amsterdam, The Netherlands, (1980).
- [14]. B.S. Randhwa, J. Mater. Chem. 10 (2000) 2847
- [15]. S. Gubbala, H. Nathani, K. Koizol, R.D.K. Misra, Physica B 348 (2004) 317.
- [16]. C. Caizer, J. Magn. Mater. 251 (2000) 304
- [17]. X.M. Liu, S.Y. Fu, J Mag. Magn. Materials 308 (2007) 61-64.
- [18]. H. Chaoquan, G. Zhenghong, Y. Xiaorui, J Mag. Magn. Materials 320 (2008) L70-L73.
- [19]. J. Smith and H.P.J. Wijn, Ferrites, Philips Technical Library Eindhoven, The Netherlands, 1959.
- [20]. K. Raj, R. Moskowitz and R. Casciari, J Mag. Material, Vol. 149, 1-2, (1995) 3398.