



ON PRODUCTION OF MAGNETIC MATERIALS HAVING $\text{NiO}_{1-x}\text{ZnO}_x\text{Fe}_2\text{O}_4$

[Mumin SAHIN, Cenk MISIRLI, Mustafa ARAS]

Abstract— In this study, characteristics and magnetic properties of magnetic materials having $\text{NiO}_{1-x}\text{ZnO}_x\text{Fe}_2\text{O}_4$ structure were investigated. Mechanical mixing of high purity NiO, ZnO and Fe_2O_3 powders were done to obtain homogenous $\text{NiO}_{1-x}\text{ZnO}_x\text{Fe}_2\text{O}_4$ powder mixture for $x=0.15$, $x=0.50$ and $x=0.85$. These powder mixtures were pressed using hydraulic press machine and then subjected to sintering at same temperatures of 1000°C for 1 hour. Obtained specimens were analysed with SEM (Scanning Electron Microscopy) imaging and EDXRF (Energy-Dispersive-X-Ray Fluorescence) technique for the investigation of structural analysis; magnetic properties was determined using VSM (Vibrating Sample Magnetometer).

Keywords— *Magnetic Materials; $\text{NiO}_{1-x}\text{ZnO}_x\text{Fe}_2\text{O}_4$; Properties*

I. Introduction

Magnetic materials have many usage areas at viewing, magnetic recording, magnetic cooling and magnetic reporting etc. in diverse subjects such as biomedical, computer technologies, energy, environmental biology, catalysts, sensors, electronically or electromagnetic interference problems. Ferrites have additional metallic ions along ferrous oxide (Fe_2O_3). Ions which united with Fe_2O_3 determine crystal structure and type of the ferrite. Hysteresis curve of material is examined for understanding magnetic characteristic and if material is suitable to applications. Soft magnetic material is more capable to magnetize and demagnetize and vice versa for hard magnetic material. In early years soft and hard terms are defined for physical properties. Today soft and hard terms have to meant easier to magnetize and harder to magnetize because they do not have to be soft or hard physically.

Prof. Dr. Mumin SAHIN
Mechanical Engineering Department, Trakya University
Edirne / TURKEY
mumins@trakya.edu.tr

Assist. Prof. Dr. Cenk MISIRLI
Mechanical Engineering Department, Trakya University
Edirne / TURKEY
cenkm@trakya.edu.tr

MSc. Mustafa ARAS
Mechanical Engineering Department, Trakya University
Edirne / TURKEY

A soft magnet has high magnetic conductivity (B_s – saturation magnetization) and low coercive force. Simply curve has smaller area. By the way hard magnetic materials which used to produce permanent magnets or hard magnets have wide hysteresis rings and high coercive force. Hard ferrite ceramic permanent magnets are widely used at electric motors and relays [1]. Ferromagnetism is defined by Neel to define magnetization of ferrites [2]. Ferrites are semiconductors and they have high electrical resistance so there won't be current vortex with magnetic field. Muhammad Ajmal and Asghari Maqsood examined AC conductivity, density, magnetic properties of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples which prepared with standard solid state reaction for different zinc concentrations [3]. In collaborative work of M.A. Gabal, Reda M.El-Shishtawy, Y.M.Al Angari $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ nano particles are synthesized with oxalate based precursor method for ($x=0, 0.2, 0.4, 0.6$) values [4]. Unchista Wongpratrat, Santi Meansiri, Ekaphan Swatsitang examined magnetic properties and local structures of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ based ($x= 0, 0.25, 0.50, 0.75, 1.00$) nano particles which prepared with hydrothermal method in aloe vera solution [5]. The increase in the Zn^{2+} concentration can cause the constant parameters to rise and led to the formation of single parameters to rise and led to the formation of single phase cubic spinel Ni-Zn ferrite and after sintering at $1,200^\circ\text{C}/2$ h, the apparent density increased according the Zn^{2+} concentration [6,7]. The specific saturation magnetization (M_s) of samples increases with the concentration of zinc ions at room temperature [8].

II. The Experimental Method

Powders prepared from NiO with high purity (Sigma Aldrich; 99,8% purity >50 nm), ZnO (Metal Oxide; >99,9%) and Fe_2O_3 powders for $x=0,15$ $x=0,50$ and $x=0,85$ mole values are mechanically mixed to create powder mixtures in homogeneous $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ structure. Molecular weights of used powders are NiO = 74,69 g/mole, ZnO = 65,39 g/mole, Fe_2O_3 = 159,70 g/mole. Powders are pressed at hydraulic press and sintered at 1000°C for 1 hour. Bulk samples produced with powder metallurgy are examined with SEM for structural analysis, analyzed EDXRF and magnetic properties are determined with VSM.

Powder Metallurgy (PM) is a production method which produces close to final product and do not need finalizing processes and allows alloys of high tech materials. PM aims to produce metallic and ceramic powders and merging these powders with various thermal and mechanic deformation principles then to convert into usable engineering parts. This conversion basically consist mixing of powders homogeneously, compressing of powder mixture in mold, atmosphere controlling to bond powder particles together and sintering at required temperature and time. Generally PM is

production method which consist homogeneously mixing powders which have different type, form and compressibility after determining % weight proportions, compressing of mixture at proper atmosphere to convert desired form with increasing density then sintering to increase strength and density [9].

For experimental study $Ni_{1-x}Zn_xFe_2O_4$ ($0 \leq x \leq 1$) $x=0,15$ $x=0,50$ and $x=0,85$ from NiO, ZnO, Fe_2O_3 powders are measured at precision scale as suitable with stoichiometry then mechanically mixed to obtain homogenous powder mixture. After mixing, powder mixtures are pressed at hydraulic press. Pressing process generally defined density increasing process of powder particles under load. Main aim of pressing after mixing is to gain raw density and strength. For this process hydraulic press is used at this experimental study. However mechanic and pneumatic presses are used for pressing process. Pressing may be done at desired temperature with additional equipment. In study pressing is executed at room temperature without any heating process. Steps of typical pressing process are shown in figure 1 [1].

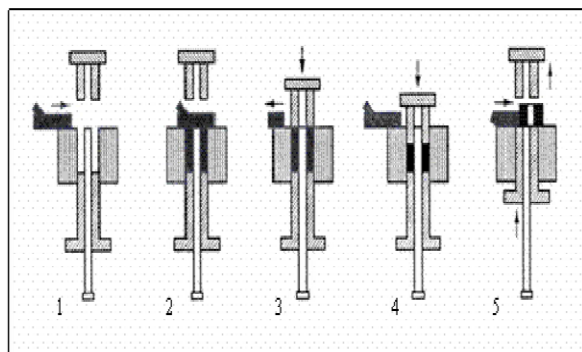


Figure 1. Steps of Pressure procedure;

1. Beginning of procedure, 2. Powder filling,
3. Beginning of Pressing, 4. Finishing Pressing,
5. Removing of Pressing samples [1]

Microstructure viewing is executed with Philips XL 30 SFEG scanning electron microscope. To define elemental content of samples EDXRF (Energy-Dispersive-X-Ray Fluorescence) analysis is executed with EDAX elemental analysis detector which connected to Philips XL 30 SFEG. To determine magnetic properties of samples VSM (Vibrating Sample Magnetometer) device is used. Electromagnet which is used for measurements can work at ± 8000 Oe magnetic field range. System software controls VSM's work and used for calibration, gathering, defining and reporting of data. Magnetic measurement of samples is executed with VSM system.

III. Results And Discussion

To gather information about physical properties of samples, weight is measured with precision scale and dimension is measured with digital compass at different steps of sample preparation. Measurements are given below as tables. Samples are coded as Composition 1 ($NiO_{0,15}ZnO_{0,85}Fe_2O_3$), Composition 2 ($NiO_{0,50}ZnO_{0,5}Fe_2O_3$), Composition 3 ($NiO_{0,85}ZnO_{0,15}Fe_2O_3$) according to their compounds. Three items are produced for each compound. But non-conforming samples which have production errors are not included in tables (Tables 2 and 3).

Table 2. Weight measurement of samples; before or after sintering

Composition / Specimen	Weight of before Pressing (g)	Weight of before Sintering (g)	Loss of weight until sintering %	Weight of after Sintering (g)	Loss of weight during sintering %	Weight of Magnetic measurement (g)	
C1	S1	1	0,9754	2,4600	0,9527	2,3273	Non-Magnetic Measurement
	S2	1	0,9741	2,5900	0,9500	2,4741	0,0924
C2	S1	1	0,9776	2,2400	0,9454	3,2938	0,0737
	S2	1	0,9808	1,9200	0,9474	3,4054	Non-Magnetic Measurement
C3	S1	1	0,9515	4,8500	0,9042	4,9711	Non-Magnetic Measurement
	S2	1	0,9797	2,0300	0,9344	4,6239	0,1062

Table 3. Size measurement of samples; before or after sintering

Composition / Specimen	Before Sintering Dimension/Height (cm)		After Sintering Dimension/Height (cm)		Reduction volume in Sintering %	
C1	S1	15,06	2,26	14,32	2,29	8,3857
	S2	15,03	2,48	14,34	2,41	11,5403
C2	S1	14,99	2,76	13,56	2,51	25,5815
	S2	15,01	2,46	13,59	2,27	24,3571
C3	S1	15,16	1,92	13,46	1,75	28,1497
	S2	15,00	2,33	13,27	2,10	29,4621

Detailed dimension and weight measurements are given above at tables 2 and 3. Sample weights are measured with 0.0001 g precision balance precision scale and dimensions are measured with 0.01 cm precision balance digital compass. Measurements are repeated and mean values of measurements are taken. In tables weight loss is visible between 1,92-4,85% range. Reason of this overflowing of powders from mold and contacting to surfaces (to the measurement devices, glove etc.) prior to sintering. Actually weight loss as low as only 0.0485 – 0.0192 grams is happened and this is an indicator of precise working during experiment. Apart from that design of mold used for pressing could be changed and samples could be kept at surface with lower adhesion, maximum care could be taken when handling with measurement devices and gloves to avoid contamination and as a result weight loss may be decreased and raw material may be used efficiently. Alongside weight loss in 2.3273% – 4.9711% range is examined during sintering because of vaporization of damp in samples and incapable of some amount of samples on aluminum plate. In tables weight losses after sintering are ranged C1<C2<C3. It is thought that situation is connected to moisture holding capacities. In dimension measurement tables, diameter/height measurement and volume decrease of samples % after pressing and after sintering. Volume decrease is visible between 8,38% – 29,4621% range relative to compounds. Volume decrease values are C1<C2<C3 in parallel to weight losses % after sintering and that supports result above.

Microstructure viewing of samples is examined with Philips XL 30 SFEG scanning electron microscope and to comparative review of particle dimension and structure 50000 times zoomed images are taken.

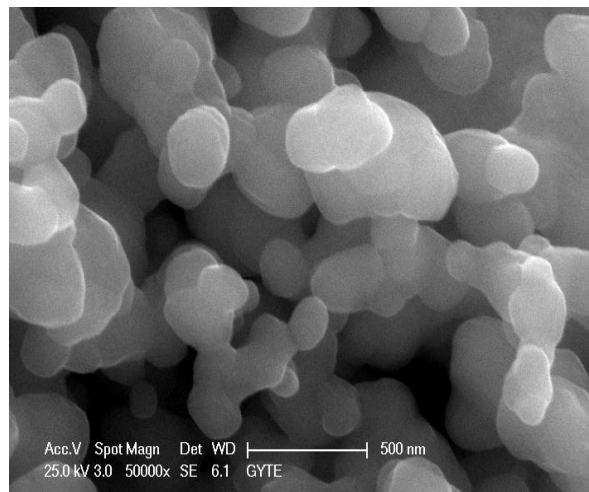


Figure 2. Composition 1 – 1000 °C – SEM viewing of Specimen 2 on 50000 zoom

200 to 500 nm particles which have recently started necking are seen at SEM photographs of Composition 1 – 1000°C – Specimen 2 in figure 2. Particle shapes are generally look like sphere despite forms apart from sphere when particle size increase.

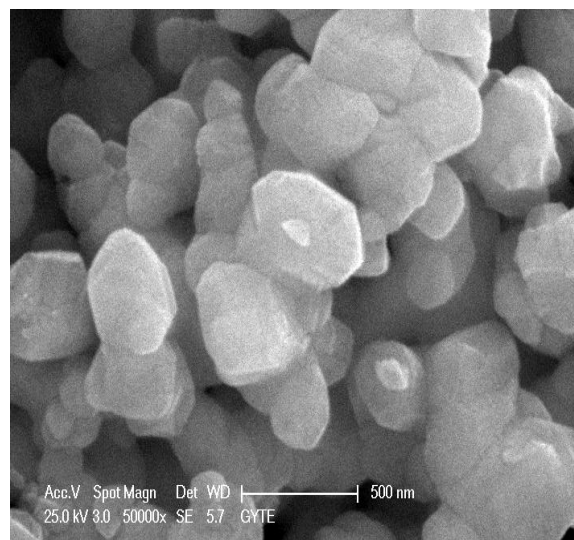


Figure 3. Composition 2 – 1000 °C – SEM viewing of Specimen 1 on 50000 zoom

200 nm particles which started to apart from spherical shape and structures which several particles are hold together at microstructure photographs of Composition 2 – 1000°C –

Specimen 1 in figure 3. Vacant areas between particles are visible.

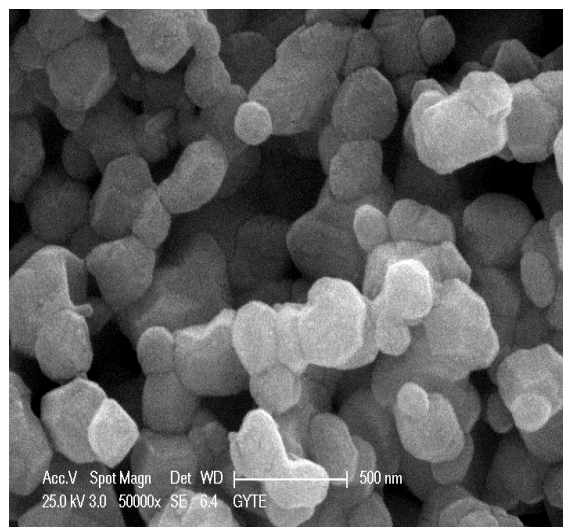


Figure 4. Composition 3 – 1000 °C – SEM viewing of Specimen 2 on 50000 zoom

100-500 nm particles which are shaped near spherical are shown at starting of necking period at SEM images of Composition 3 – 1000 °C – Specimen 2 in figure 4. Particles which are at further periods of necking are visible despite they are uncommon. Vacancies between particles up to 1µm are evident.

However, the results show that, with increasing Zn content the grain size increased and the ferrite samples exhibit an exaggerated continuous grain growth with grains containing some fine pores.

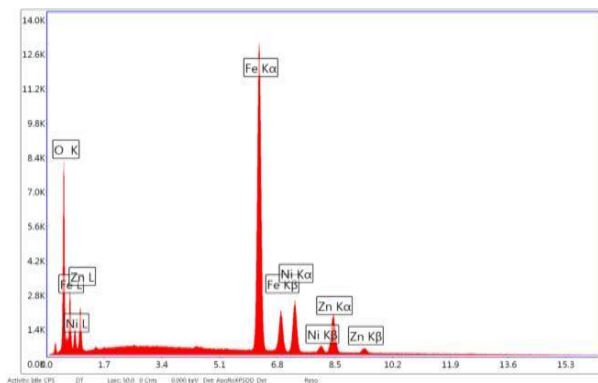


Figure 5. Composition 2 – 1000 °C – EDXRF Analysis Graphic of Specimen 1

When EDXRF graph in figure 5 are examined Ni, Zn, O, Fe peaks are visible and very little unidentified peaks are available because of impurities in samples at ppm level. Reasons of these impurities are impurity in raw material and impurity from environment because of conditions of working.

Atomic and weight % contents of samples with EDXRF are shown in tables 4 and 5.

Table 4. Atomic Content (%) of Selected Samples after EDXRF Analysis

Code of Specimen	Ni (%)	Zn (%)	O (%)	Fe (%)
C1 – S2	1.99	12.27	54.92	30.81
C2 – S1	7.17	7.45	53.96	31.42
C3 – S2	11.44	2.12	55.6	30.84

Table 5. Weight Content (%) of Selected Samples after EDXRF Analysis

Code of Specimen	Ni (%)	Zn (%)	O (%)	Fe (%)
C1 – S2	3.32	22.8	24.97	48.91
C2 – S1	11.94	13.81	24.48	49.76
C3 - S2	19.63	4.06	25.99	50.32

Magnetization measurement of samples produced during study is executed at room temperature with Vibrating Sample Magnetometer (VSM) device. Information about magnetic properties can be gained with magnetization measurement with VSM device.

The obtained results of measurements are given in Table 6 and 7, the results of VSM is given in Figure 6.

Table 6. For Ni_{1-x}Zn_xFe₂O₄ (0 ≤ x ≤ 1) Maximum Magnetic Moment (M_s→emu/g) Measurement and Magnetic Area Measurement (H→Oe)

C1		C2		C3	
S1	S2	S1	S2	S1	S2
Non-Magnetic Measurement	M _s =45,1762	Non-Magnetic Measurement	Non-Magnetic Measurement	Non-Magnetic Measurement	M _s = 3,4197
	H=7734,10				H=7817,10

Table 7. For $Ni_{1-x}Zn_xFe_2O_4$ ($0 \leq x \leq 1$) in negative direction Maximum Magnetic Moment ($M \rightarrow emu/g$) Measurement and Magnetic Area Measurement ($H \rightarrow Oe$)

C1		C2		C3	
S1	S2	S1	S2	S1	S2
Non-Magnetic Measurement	$M = -44,8218$	$M = -50,4371$	Non-Magnetic Measurement	Non-Magnetic Measurement	$M = -3,3263$
	$H = -6906,10$	$H = -7721,50$			$H = -7687,90$

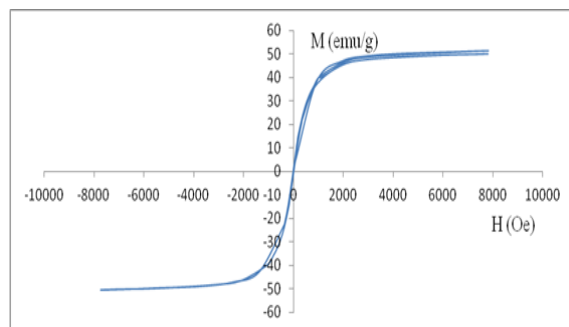


Figure 6. Composition 2 - 1000 °C - Results of VSM Measurement for Specimen 1

Fig. 6 shows the room temperature hysteresis loops for $Ni_{1-x}Zn_xFe_2O_4$ compositions at magnetic field strength 8kOe. The curves shape exhibit ferrimagnetic character of the investigated samples. Appearance of the sigmoid-shape M-H curve corresponds to the first appearance of significant ferromagnetic order of the samples with single-phase purity and a sufficient number of grains beyond a critical size being the reasoning conditions for the appearance. The magnetic properties were elucidated from the hysteresis data and tabulated in Table 6 and 7.

IV. Conclusions

Production of nickel zinc ferrite ceramic magnet samples is done successfully. Following results are come to conclusion:

- All samples show ferrimagnetic behavior.
- The results indicate that higher concentrations of Ni^{2+} can influence both the microstructure and the magnetic properties of the material.

- On the other hand, magnetization increases at low temperatures with Zn substitution up to $x = 0.5$ due to the spin canting effect occurring in the samples.
- Appearance of the sigmoid M-H curve shape indicates that all these conditions have been satisfied.

Acknowledgment

The authors would like to thank to Istanbul Technical University, Gebze High Technology Institute, Kocaeli University and Trakya University-Turkey for the their help in experimental part of the study.

References

- [1] M. Aras, "Malzemelerin Manyetik Açidan Sınıflandırılması", Graduate School of Natural Applied Sciences of Trakya University Msc. Dissertation, Edirne, Turkey, 2012.
- [2] T. Yılmaz, "Saçtırma Tekniğiyle Hazırlanan Kobalt İnce Filmlerinin Manyetik Karakterizasyonu", Gebze High Tech. Inst. Eng. and Graduate School of Natural Applied Sciences Physics Department, 2008.
- [3] M. Ajmal, A. Maqsood, "AC Conductivity, Density Related and Magnetic Properties of $Ni_{1-x}Zn_xFe_2O_4$ Ferrites With The Variation of Zinc Concentration", Materials Letters, Vol. 62, 2008, pp.2077–2080.
- [4] M.A. Gabal, R. M.El-Shishtawy, Y.M. Al Angari, "Structural and magnetic properties of nano-crystalline Ni–Zn ferrites synthesized using egg-white precursor", Journal of Magnetism and Magnetic Materials, Vol. 324, 2012, pp. 2258–2264.
- [5] U. Wongpratad, S. Meansiri, E. Swatsitang, "Local structure and magnetic property of $Ni_{1-x}Zn_xFe_2O_4$ ($x = 0, 0.25, 0.50, 0.75, 1.00$) nanoparticles prepared by hydrothermal method", Microelectronic Engineering, Vol. 126, 2014, pp. 19–26.
- [6] Ana Cristina F. M. Costa, Márcio R. Morelli, Ruth H. G. A. Kiminami, Microstructure and magnetic properties of $Ni_{1-x}Zn_xFe_2O_4$ synthesized by combustion reaction, Journal of Materials Science, Vol. 42:3, 2007, pp. 779–783.
- [7] M. Rahimi, P. Kameli, M. Ranjbar, H. Hajhashemi, H. Salamati, The effect of zinc doping on the structural and magnetic properties of $Ni_{1-x}Zn_xFe_2O_4$, J Mater Sci, Vol. 48, 2013, pp. 2969–2976.
- [8] Yin Liu, Jian-jun Li, Fan-fei Min, Jin-bo Zhu, Ming-xu Zhang, Microwave-assisted synthesis and magnetic properties of $Ni_{1-x}Zn_xFe_2O_4$ ferrite powder, Journal of Magnetism and Magnetic Materials, Vol. 354, 2014, pp. 295–298.
- [9] B.Yalçın, "Toz Metalurjisi Yöntemiyle İmal Edilen Titanyum Alaşımı İmplantların Temel Özelliklerinin Araştırılması", Graduate School of Natural Applied Sciences of Süleyman Demiral University, Mech. Eng. Dept., Isparta, 2007.