Effect of Chemical Reaction Temperature on Magnetic Properties of NiCuZn Ferrites

Neelam S. Shinde[1,2], Sujata S. Khot[1,2], Nathani Basavaiah[3], Shrikant C. Watawe[4], and Milind M. Vaidya[5]

[1]D. B. J. College, Chiplun 415605, India
[2]Smt. Chandibai Himathmal Mansukhani College, Ulhasnagar 414005, India
[3]Indian Institute of Geomagnetism, New Panvel 410218, India
[4]P. D. Karkhanis College, Ambernath 421501, India
[5]Vedanta College of Management and Information Technology, Vitthalvadi 411004, India

$Ni_{0.5}Cu_{x/2}Zn_{(0.5-x/2)}Fe_2O_4$ (where x = 0.3, 0.4, 0.5, and 0.6) ferrites were prepared at different chemical reaction temperatures (100 °C, 125 °C, and 150 °C) and then were further sintered using domestic microwave oven. X-ray diffraction revealed the ferrite phase formation and proved that chemical reaction temperature affects the structural properties. Magnetic properties, such as saturation magnetization, coercivity, Curie temperature, and normalized susceptibility were found to be dependent not only on composition, but also on chemical reaction temperature. Grain size was found to be in range of 41.866–200.909 nm.

***Index Terms*— Coercivity, Curie temperature, normalized saturation magnetization, susceptibility.**

I. Introduction

THE trends of miniaturizing the electronic devices result in multilayer ferrite chip inductor (MLFCI) components. The traditional wire wound inductors can be miniaturized to a certain limit and lack of magnetic shielding of these wire wound components lead to the development of MLFCI. Ferrite chip inductors are one of the important components for the latest electronics products, such as cellular phones, video cameras, notebook computers, hard and floppy drives [1], and so on. At present, NiCuZn ferrites have been the dominant materials for MLFCI due to their low-sintering temperature and good electromagnetic properties [2]. In addition, NiCuZn ferrites have better high-frequency properties compared with that of MnZn ferrite and low-densification temperatures than NiZn ferrites [3].

The synthesis of ferrites can be carried out using different methods, such as sol gel, auto combustion, microwave assisted combustion, chemical method, ceramic method, and so on. The chemical reaction temperature (C.R.T.) seems to be very important parameter in a chemical process as the reaction kinematics in a chemical process depends on it [4]. The C.R.T. also affects the molecular level mixing useful in obtaining desired magnetic properties. This paper is focused on a combination of lower chemical reaction temperature followed by microwave sintering for the completion of solid state reaction that could be useful for obtaining nanoferrites with required parameters.

II. Experimental Technique

A. Synthesis

NiCuZn ferrite powders, having general formula $Ni_{0.5}Cu_{x/2}Zn_{(0.5-x/2)}Fe_2O_4$ (where $x = 0.3$, 0.4, 0.5, and 0.6) have been prepared at three different C.R.T. followed by sintering using microwave oven operating at maximum power output of 700 W (Godrej Microwave Oven, Model—GMS 17M07 WHGX). Nickel nitrate, ferric nitrate, zinc nitrate, and copper nitrate (all AR grade) were used as starting materials. The stoichiometric proportions of nitrates were weighed and added in 100 mL of distilled water to produce an aqueous solution. The solution was kept in paraffin oil bath at three different C.R.T. 100 °C, 125 °C, and 150 °C with constant stirring using the magnetic stirrer. The process was carried out for 3 h in which nitrous fumes were released, which could be observed directly. The solution was then obtained in the form of slurry. It was observed that slurry formed at 150 °C was highly viscous, compared with the slurry formed at 100 °C, where as the viscosity of slurry formed at 125 °C was moderate. The slurry was directly transferred to the microwave oven. The irradiation was given for 20–50 min at maximum power in the form of pulses and the release of nitrous gas was observed. The irradiation process was stopped when nitrous gas was evaporated completely. The obtained ferrite powder was then crushed in agate mortar.

B. Characterization

X-ray diffraction (XRD) measurements were carried out using D8 Advance by M/s Bruker AXS, GmbH, Germany. Saturation magnetization measurements were carried out using MicroMag 2900—alternating gradient magnetometer (Princeton Measurements Corporation). Curie temperature was measured using AGICO KLY-45 Kappabridge. Microstructures were taken using FEG-SEM, model JSM-7600F.

III. Results and Discussion

A. Structural Evaluations

The XRD patterns shown in Fig. 1 (for sample $x = 0.4$) confirms the formation of NiCuZn ferrites. Magnetic properties are structure-dependent, while structure depends on preparation techniques. Many undesired peaks are observed in Fig. 1, for samples prepared at C.R.T. 100 °C showing the secondary phases whereas samples prepared at C.R.T.

Manuscript received February 20, 2014; revised May 18, 2014; accepted June 3, 2014. Date of current version November 18, 2014. Corresponding author: N. S. Shinde (e-mail: neelamshinde1976@gmail.com).
Digital Object Identifier 10.1109/TMAG.2014.2329328

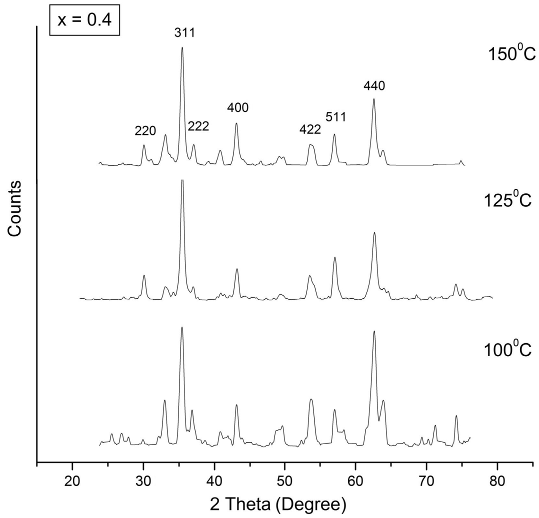

Fig. 1. XRD for $x = 0.4$.

TABLE I
SATURATION MAGNETIZATION (M_s), COERCIVITY (H_c), CURIE TEMPERATURE (T_c), BULK SUSCEPTIBILITY, AND GRAIN SIZE WITH RESPECT TO C.R.T. AND COMPOSITION (x)

C.R.T. (^{0}C)	Comp. x	M_s (emu/gm)	H_c (O_e)	T_c (^{0}C)	Bulk suscep.	Grain size (nm)
100	0.3	4.279	92.03	427	0.149	200.90
	0.4	18.61	64.91	431	0.257	181.66
	0.5	14.24	97.12	450	0.189	88.18
	0.6	9.696	84.99	474	0.180	89.39
125	0.3	23.77	71.14	418	0.443	41.86
	0.4	50.37	59.32	426	0.493	89.39
	0.5	28.04	80	470	0.504	72
	0.6	33.65	61.86	490	0.476	81.81
150	0.3	20.45	132.5	418	0.336	79.16
	0.4	24.48	76.69	430	0.350	96.96
	0.5	14.83	100.7	447	0.236	56.81
	0.6	15.89	90.18	470	0.278	51.51

125 °C and 150 °C show no extra peaks corresponding to any secondary phases. This can be attributed to chemical kinematics. Increasing C.R.T. increases reaction rates because of the disproportionately large increase in the number of high-energy collisions. Collisions results in a reaction if the particles collide with enough energy to get the reaction started. This minimum energy required is called the activation energy for the reaction [4]. In addition, the broadening of 311 peaks depicts the formation of nanocrystallites, which is the result of microwave sintering.

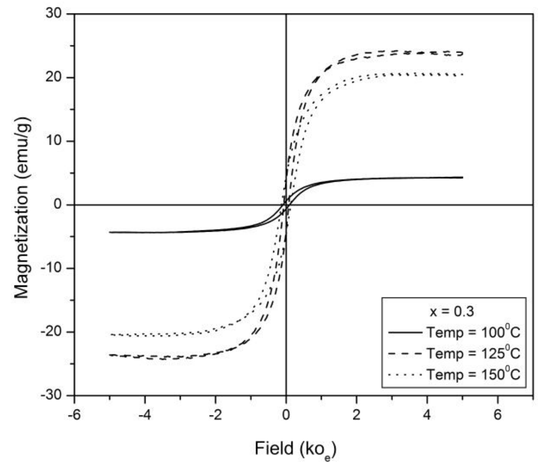

Fig. 2. Hysterisis curve for $x = 0.3$.

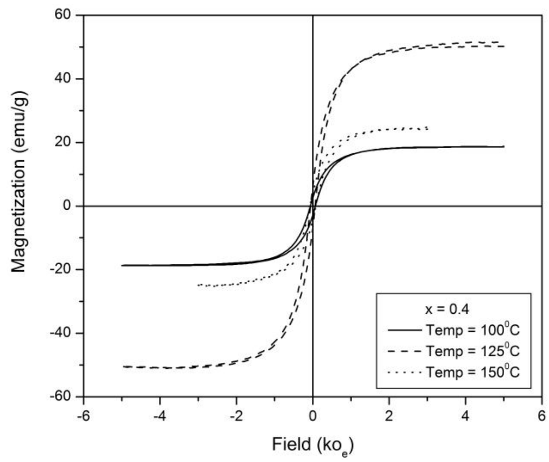

Fig. 3. Hysterisis curve for $x = 0.4$.

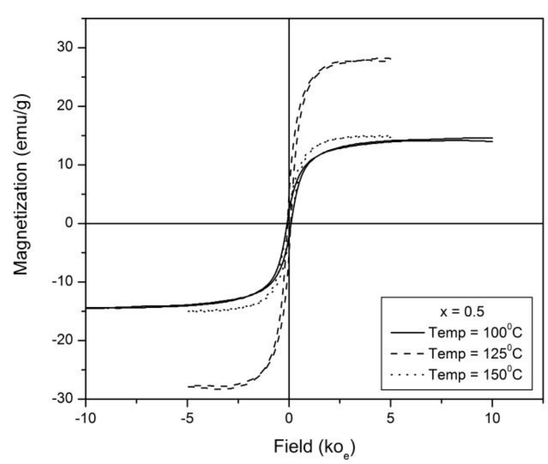

Fig. 4. Hysterisis curve for $x = 0.5$.

B. Saturation Magnetization (M_s)

Magnetization in ferrites is strongly influenced by the site preference of ions in the spinel lattice. Substitution for Zn^{2+} ions by Cu^{2+} ions in NiCuZn ferrite increases the saturation magnetization up to concentration $x = 0.4$ and then decreases with further increase in composition, i.e., $x > 0.4$ (Table I). The variation in M_s with composition can be explained on the basis of the exchange interaction between the ions at the tetrahedral (A) and octahedral (B) sites in the crystallographic lattice; besides this intrinsic factor, M_s is also influenced by extrinsic factors, such as microstructure and densities of ferrites [5]. Variation in M_s, with respect to C.R.T., as shown

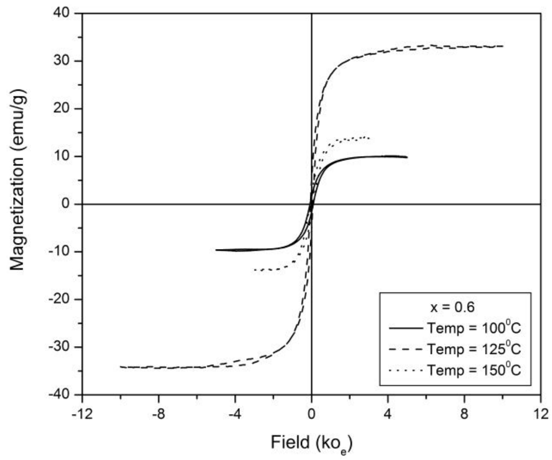

Fig. 5. Hysterisis curve for $x = 0.6$.

in Figs. 2–5 shows higher M_s values for all compositions prepared at C.R.T. 125 °C and least values at C.R.T. 100 °C. The C.R.T. shows its effect on saturation magnetization.

C. Coercivity (H_c)

All samples exhibit moderate coercivity values as shown in Table I. Maximum coercivity values of 132.5, 76.69, 100.7, and 90.18 Oe were obtained for composition $x = 0.3$, 0.4, 0.5, and 0.6, respectively, prepared at C.R.T. 150 °C, which might be due to an extrinsic effect associated with a favorable microstructure in the sample [6]. Since coercivity is the microstructural property, it depends on defects, strains, nonmagnetic atoms, and so on in the material. However, least values of coercivity 71.14, 59.32, 80, and 61.86 Oe were obtained for composition $x = 0.3$, 0.4, 0.5, and 0.6, respectively, prepared at C.R.T. 125 °C. This might be due to the higher grain size, as it is known that, H_c decreases with increasing grain size.

D. Curie Temperature (T_c)

The Curie temperature was found to increase with increase in Cu^{2+} ions from $x = 0.3$ to 0.6 for all C.R.T., as shown in Table I. This increase in Curie temperature could be attributed to the substitution for Zn^{2+} ions by Cu^{2+} ions. The magnetic moment of Cu^{2+} being higher than that of Zn^{2+}, substitution of Cu^{2+} in place of Zn^{2+} results in an increase in the exchange interaction between the A and B sublattices. Therefore, the thermal energy required to offset the spin alignment increases, increasing the Curie temperature. However, in Figs. 6–9 no noticeable change was observed with respect to C.R.T.

E. Normalized Susceptibility (χ_{AC})

In Figs. 6–9, it is observed that temperature dependence of the normalized susceptibility for all the samples remained independent of temperature up to certain range and then dropped to zero. This suggests that all the samples exhibit multidomain structure [7]. Whereas, bulk susceptibility values (Table I), were found to be higher in samples prepared at C.R.T. 125 °C and lower in samples prepared at C.R.T. 100 °C,

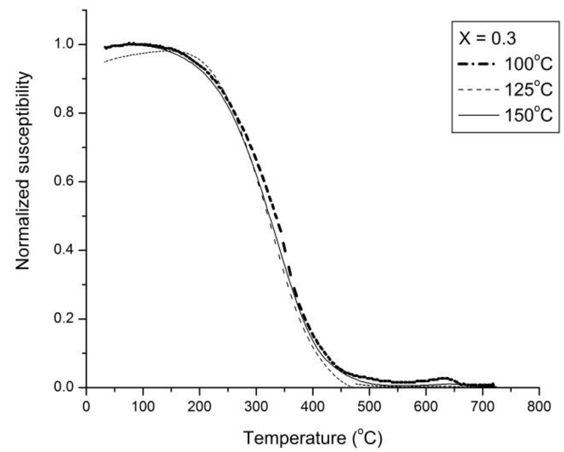

Fig. 6. Normalized susceptibility for $x = 0.3$.

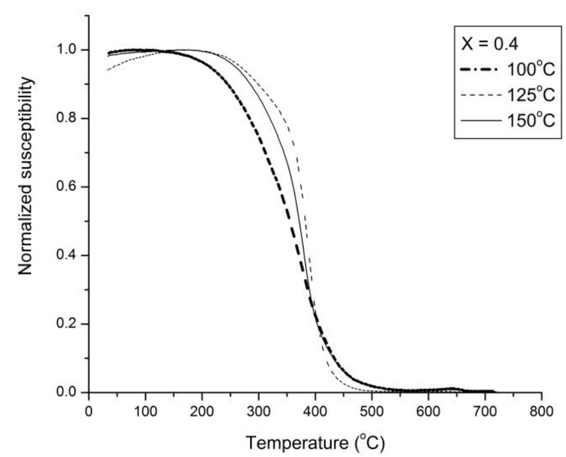

Fig. 7. Normalized susceptibility for $x = 0.4$.

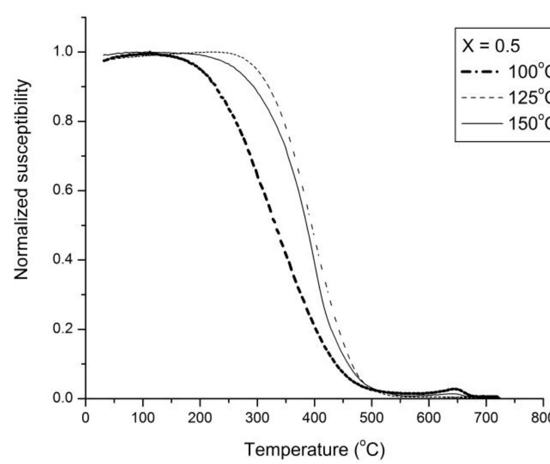

Fig. 8. Normalized susceptibility for $x = 0.5$.

which indicates that samples prepared at C.R.T. 125 °C, possess higher magnetization.

F. Grain Size

Fig. 10 shows the microstructure of sample $x = 0.5$ prepared at C.R.T. 100 °C. Grain size is found to be in range

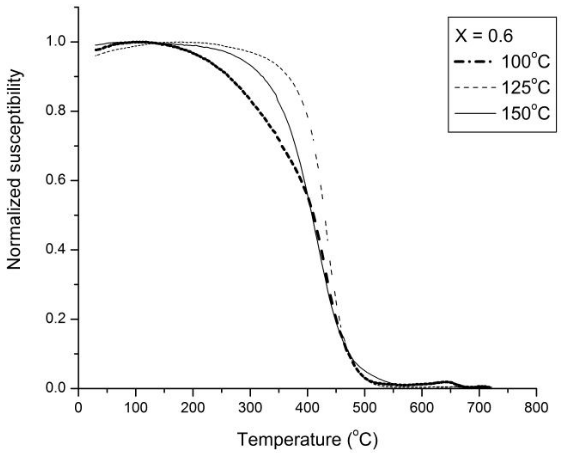

Fig. 9. Normalized susceptibility for $x = 0.6$.

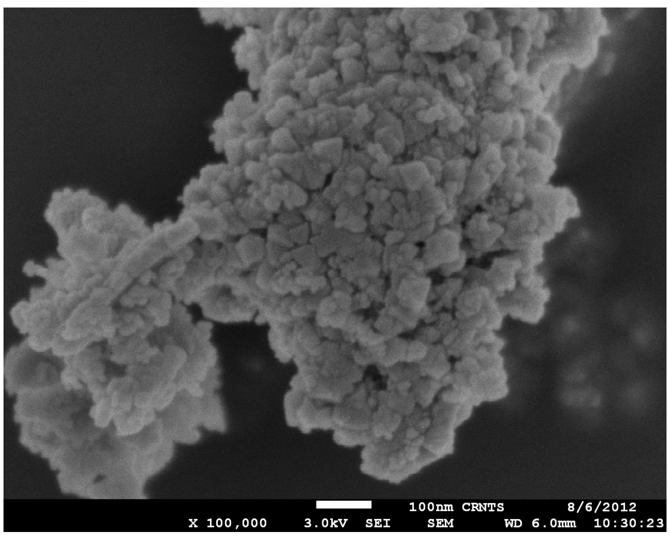

Fig. 10. SEM of sample $x = 0.5$ and C.R.T. = 100 °C.

41.86–200.90 nm (Table I). The grain size of ferrites is related to the chemical composition, the preparation conditions, the cell volume, the secondary phases, and the glomeration behavior of particles [8]. Maximum grain size of 200.909 nm is found for composition $x = 0.3$ prepared at 100 °C and least grain size 41.866 nm is found for same composition ($x = 0.3$) prepared at 125 °C, hence C.R.T. shows its effect on grain size. Except for samples $x = 0.3$ and 0.4 prepared at C.R.T. 100 °C, the grain size of all other samples is found to be <100 nm, which is the effect of microwave sintering resulting in nanoparticles.

IV. Conclusion

Chemical reaction temperature of 125 °C results in good structural and magnetic properties compared with 100 °C and 150 °C.

The effect of chemical reaction temperature should be considered while formation of ferrites, as it affects the structural properties which in-turn affects the magnetic properties of ferrites.

A combination of lower chemical reaction temperature for molecular level mixing followed by microwave sintering for the completion of solid state reaction could be useful for obtaining nanoferrites with required parameters.

Acknowledgment

The authors would like to thank the Principal Dr. S. R. Joshi and Vice Principal Dr. S. N. Gawale from D. B. J. College, Chiplun, India, for providing experimental facilities and encouragement, Prof. D. C. Kothari from the Department of Physics, Mumbai University, Mumbai, India, for providing access to e-journals, Dr. B. B. Kale, S. K. Apte, and S. Naik from the Center for Materials for Electronics Technology, Pune, India, for providing XRD facility, and P. Das and A. Mohamad from the Indian Institute of Geomagnetism, Panvel, India, for providing magnetic measurements.

References

[1] T. Krishnaveni, B. R. Kanth, V. S. R. Raju, and S. R. Murthy, "Fabrication of multilayer chip inductors using Ni–Cu–Zn ferrites," *J. Alloys Componnds*, vol. 414, nos. 1–2, pp. 282–286, Apr. 2006.

[2] J. Z. Msomi, T. Moyo, and T. B. Doyle, "Magnetic properties of bulk and nanosized (Zn, Cu, $Cd)_{0.5}Ni_{0.5}Fe_2O_4$ ferrites," *J. Magn. Magn. Mater.*, vol. 310, no. 2, pp. 2534–2536, Mar. 2007.

[3] D. Stoppels, "Developments in soft magnetic power ferrites," *J. Magn. Magn. Mater.*, vol. 160, pp. 323–328, Jul. 1996.

[4] M. George, A. M. John, S. S. Nair, P. A. Joy, and M. R. Anantharaman, "Finite size effects on the structural and magnetic properties of sol–gel synthesized $NiFe_2O_4$ powders," *J. Magn. Magn. Mater.*, vol. 302, no. 1, pp. 190–195, Jul. 2006.

[5] M. C. Dimri, A. Verma, S. C. Kashyap, D. C. Dube, O. P. Thakur, and C. Prakash, "Structural, dielectric and magnetic properties of NiCuZn ferrite grown by citrate precursor method," *Mater. Sci. Eng., B*, vol. 133, nos. 1–3, pp. 42–48, Aug. 2006.

[6] J. F. Wang, C. B. Ponton, R. Grössinger, and I. R. Harris, "A study of La-substituted strontium hexaferrite by hydrothermal synthesis," *J. Alloys Compounds*, vol. 369, nos. 1–2, pp. 170–177, Apr. 2004.

[7] B. P. Ladgaonkar, P. N. Vasambekar, and A. S. Vaingankar, "Effect of Zn^{2+} and Nd^{3+} substitution on magnetisation and AC susceptibility of Mg ferrite," *J. Magn. Magn. Mater.*, vol. 210, nos. 1–3, pp. 289–294, May 2000.

[8] J. Jing, L. Liangehao, and X. Feng, "Structural analysis and magnetic properties of Gd-doped Li-Ni ferrites prepared using rheological phase reaction method," *J. Rare Earths*, vol. 25, no. 1, pp. 79–83, Feb. 2007.