

Microstructure and electromagnetic properties of microwave sintered CoCuZn ferrites

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ABSTRACT

Co-Cu-Zn ferrite material has been extensively used in multilayer chip inductors because of their good electromagnetic properties at higher frequencies and low sintering temperatures. In this research work, a comparative study on Co-Cu-Zn ferrite prepared from two different routes is reported. The two different routes are conventional ceramic sintering method (CS) and microwave sintered (MS) method. The former route is most commonly used while the latter one is now gaining popularity in sintering processes. The work highlights that the sintering temperature and time were significantly reduced from 4 h and 1250 °C for the CS process to 20 min and 900 °C for MS process. Moreover, microwave sintering also improves the physical and electromagnetic properties of ferrite

Keywords: ferrite; Microwave-sintering; Microstructure; Electro-magnetic; inductors

1. INTRODUCTION

Spinel ferrites exhibit variations in structural, electrical and magnetic properties which are dependent on several factors such as method of preparation, substitution of cations, microstructure, etc. Co-Cu-Zn ferrite materials have been extensively studied for multilayer chip inductor (MLCI) applications because of their good electrical and magnetic properties at higher frequencies and low sintering temperatures [1-3]. In these applications, ferrites need to be sintered at temperatures less than 950 °C in order to get co-fired with silver internal electrode during the manufacturing process of MLCIs. The conventional sintering technique (CS) though cheaper and easier route is not suitable route for MLCI application of ferrite. It is because of the requirement of the high sintering temperature ($T_s > 900$ °C) and longer sintering time ($t_s > 5$ h) required in CS method. The addition of fluxes such as Bi₂O₃, PbO, V₂O₅ and glass can promote the low-temperature [4-6], but it is still hard to obtain the ferrites with desired electromagnetic properties at low-temperatures.

Now - a - days, microwave sintering method is becoming popular amongst the different preparation routes of ferrites, especially in overcoming the limitation of chemical route synthesis of ferrites, which are also sintered at low temperatures. Like the chemical route ferrites, MS ferrites are also being sintered at a low sintering temperature (< 960 °C) and mainly without any aid of fluxes. The advantage of MS route is that it rules out any chances of finding any intermediate phase or unreacted phase. Microwave sintering method can be termed as purely physical method of preparation because during preparation neither chemical parameters are required to be regulated nor knowledge of chemistry is essential. The

microwave sintering technique also has unique advantages over conventional sintering technique. The main advantage of microwave sintering is high post sintering density and low heat losses during the ferrite formation and rare possibility of formation of microstructural defects like inter and intra granular pores and cracks due to micro-strain or stress, which is otherwise more probable to occur in conventional sintering [7-10]. The essential difference in the microwave and conventional sintering process is in the heating mechanism. In conventional sintering, heat is generated by external heating elements and then it diffuses into the test sample via radiation, conduction and convection producing high temperature gradients and internal stress [6]. In microwave sintering, the heat is generated internally within the test sample, by rapid oscillation of dipoles at microwave frequencies [11], instead of diffusion from external sources. As a result of this internal and volumetric heating, it is possible to sinter the materials rapidly and uniformly. So the microwave sintering technique is expected to prepare the high-permeability Co-Cu-Zn ferrites at relatively low sintering temperatures. The same is reported earlier for other microwave ferrite [12,13]. In this paper, the low-sintering temperature Co-Cu-Zn ferrite, $\text{Co}_{0.35}\text{Cu}_{0.05}\text{Zn}_{0.60}\text{Fe}_{1.98}\text{O}_{4-\delta}$, was prepared using microwave sintering technique and the microstructure and electromagnetic properties are investigated and compared with CS samples.

2. EXPERIMENTAL PROCEDURE

Co-Cu-Zn ferrites of the cubic spinel structure having the general formula $\text{Co}_{0.35}\text{Cu}_{0.05}\text{Zn}_{0.60}\text{Fe}_{1.98}\text{O}_{4-\delta}$ was prepared employing the conventional double sintering and microwave sintering methods using analytical grade CoO, CuO, ZnO and Fe_2O_3 . The stoichiometric proportions of these constituent oxides were weighed, intimately mixed and the resulting powders were ball milled using a planetary ball mill with agate balls in aqueous medium for 20 h. The slurry was dried and loosely pressed into cakes using a hydraulic press. These cakes were pre-sintered at a temperature of 800 °C for 4 h in closed alumina crucibles. The pre-sintered cakes removed from the furnace were crushed and ball milled in an aqueous medium in agate bowls with agate balls for another 30 h to obtain fine particle size. These slurries after drying were sieved to obtain a uniform particle size. The green powder thus obtained was then pressed using a suitable die into two sets of toroids with a hydraulic press at a pressure of 200 MPa using 2 % PVA solution as a binder. The green pressed samples were divided into two batches (A and B): one was processed with CS process while another with the MS process. In CS process, the samples (batch A) were sintered in electrical programmable furnace at 1250 °C for 4 h and were cooled to room temperature at the rate of 80 °C h⁻¹. Another set (set B) of the green pressed samples were subjected to the microwave furnace. The green pressed samples were finally sintered at 950 °C for 20 min. The cooling rate was kept same.

The single spinel phase formation for both the ferrites was confirmed by x-ray diffraction (XRD) with Cu K_α radiation. The density of the materials was measured using Archimede's method. The microstructure of the fracture surfaces was studied by Scanning electron microscopy (SEM). The HP LCR meter was used to measure the frequency dependence of dielectric properties from 100 Hz to 1 MHz, and also to measure the temperature dependence of magnetic permeability from 30 to 250 °C. The magnetic characteristics were measured with VSM-Vibrating sample magnetometer (VSM)

3. RESULTS AND DISCUSSION

Fig. 1. shows the XRD patterns for the samples sintered by the microwave and conventional sintering techniques. Both the XRD show a single-phase formation with spinel structure. No other phase was detected.

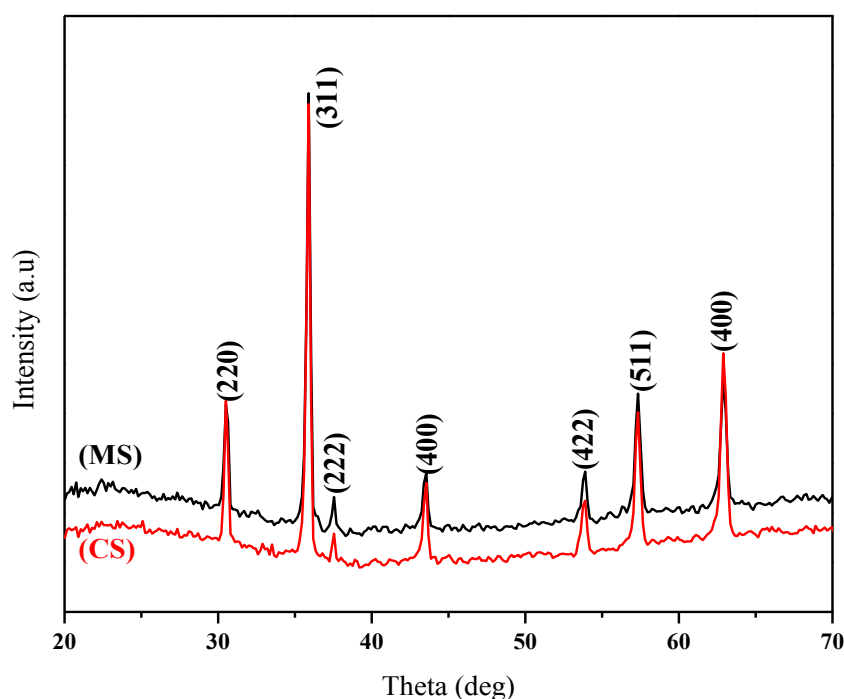


Fig. 1. XRD patterns of Co-Cu-Zn ferrite samples sintered by Microwave sintering (MS) and Ceramic (CS) routes.

The average grain size for the MS sample as estimated from the SEM photographs has been compared with that of the CS sample and it is found that the MS processed samples have much larger grains. The Fig. 2 depicts the microstructures of the MS and CS samples. It can be seen that the average grain size of MS sample is lying in the range 2.2-4.4 μm , whereas for of CS sample it falls in 1.3-2.5 μm range. The Fig. 2 also reveals that MS sample has a denser structure than CS samples.

The density for CS sample is 94.2 % while that for MS sample is 98 % of calculated X-ray density. The DC electric resistivity is an important property of low-temperature sintered (MS) ferrite for MLCI applications. The d.c. resistivity for the MS sample is of the order of 10^{10} , which is 10^3 times higher than that of the CS sample for which the resistivity is of order of 10^7 . The measurement was done at room temperature using Kiethley's meter.

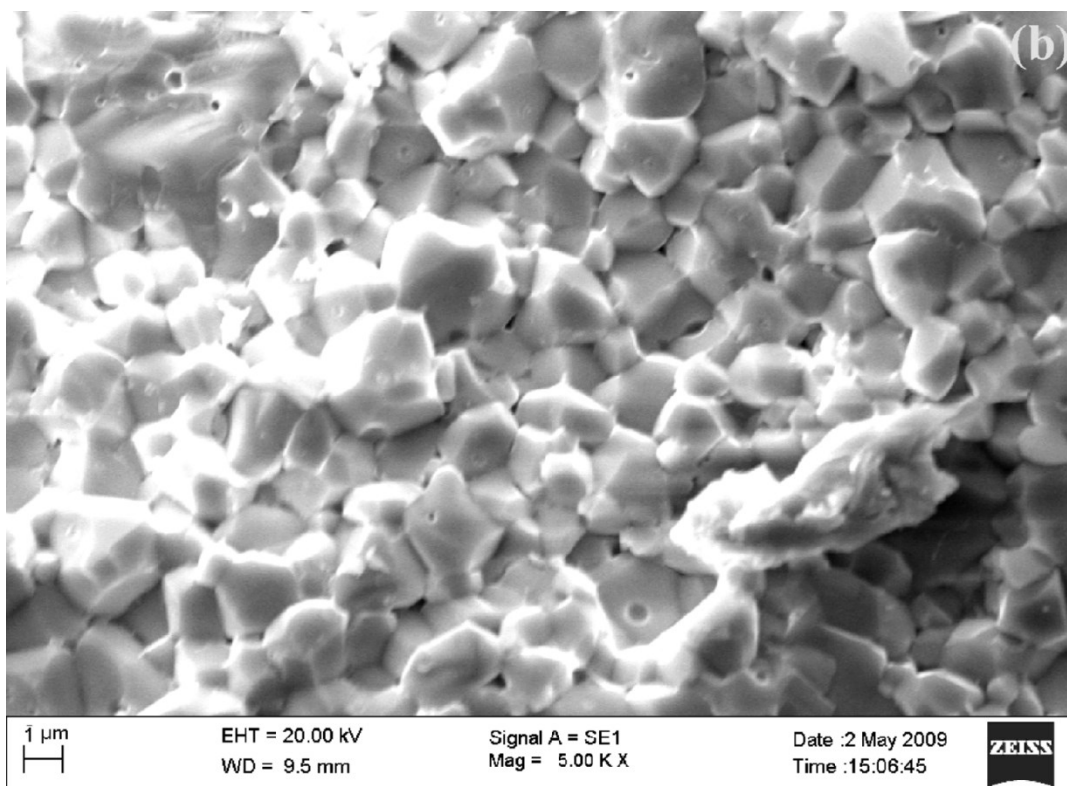
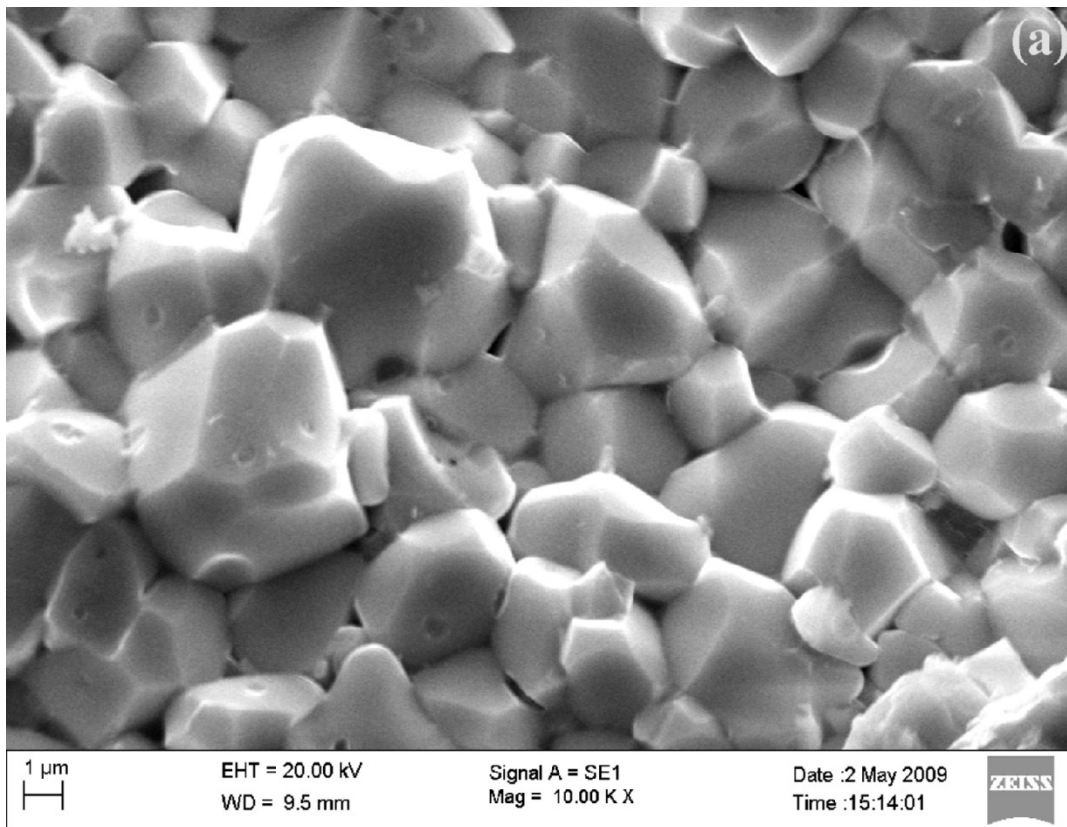


Fig. 2. SEM photographs of Co-Cu-Zn ferrite materials processed by (a) MS process and (b) CS process.

The dielectric properties such as dielectric constant (ϵ') and dielectric loss ($\tan \delta$) are important parameters for multilayer chip inductors used in high frequency range. The frequency dependence of dielectric constant and loss tangent for Co-Cu-Zn ferrite samples prepared by CS and MS process are shown in Fig. 3.

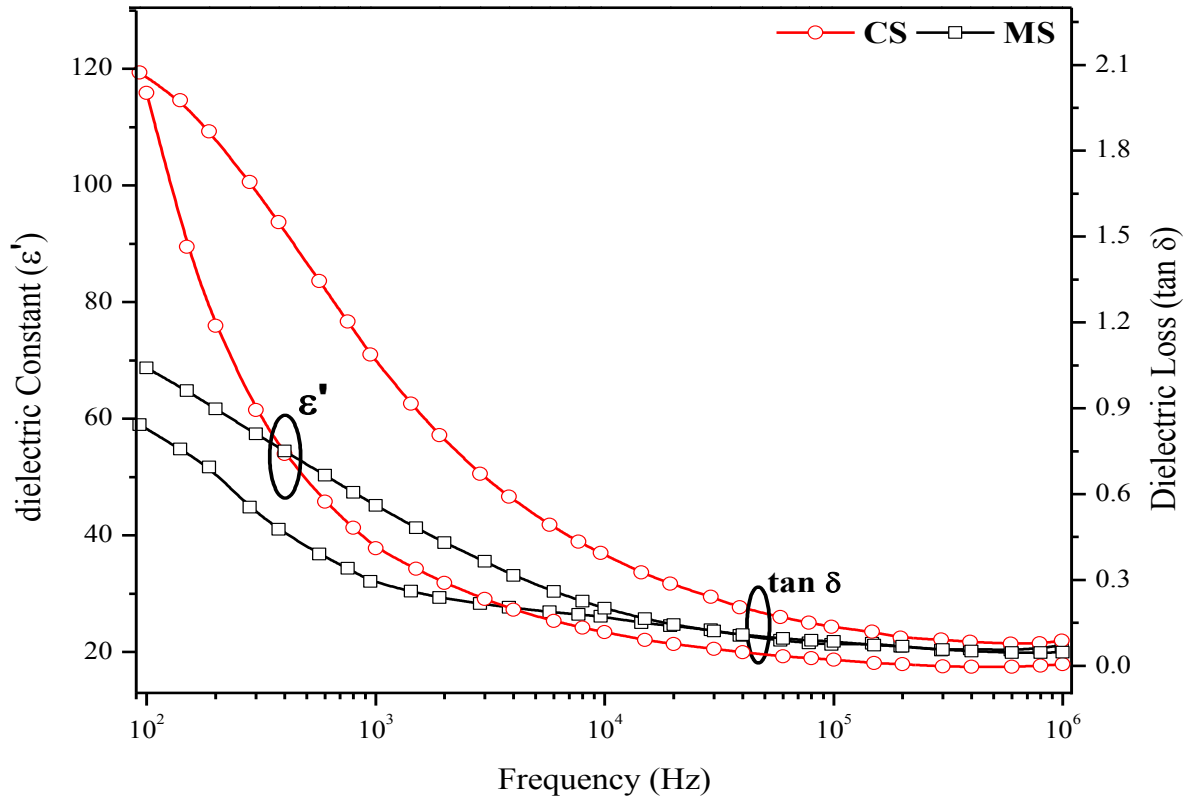


Fig. 3. Frequency dependence of dielectric constant and dielectric loss for Co-Cu-Zn ferrite samples prepared by CS and MS techniques.

The plots show that the dielectric constant and loss tangent decrease with increasing frequency. It can be seen from the figure that the MS samples has larger dielectric constant and smaller loss compared to CS samples. The dense structure of the MS sample, as confirmed by SEM result, indicates less air-holes, leading to the larger dielectric constants. Simultaneously, the MS sample show lower dielectric loss which can be attribute to rare possibility of Fe^{2+} content in the materials [14-16]. In the MS process, the shorter sintering time restrain the evaporation of O^{2-} ions, and leading to the less chances of forming Fe^{2+} content in the material. In CS method the formation of Fe^{2+} is more likely. Therefore dielectric loss in MS lower when compared to the CS sample. In fact for a good quality ferrite, the formation of Fe^{2+} must be inhibited but it becomes inevitable in CS method. This again justifies the advantage of MS processed ferrite over CS route.

The initial permeability (μ_i) as the function of temperature (at constant frequency, 10 kHz) from room temperature to Curie point was also studied. The temperature variation of magnetic initial permeability (μ_i) for both samples is shown in Fig. 4. It suggests that MS

sample has larger magnetic permeability than the CS sample. The magnetic initial permeability for the material is expected to be strongly depend on the microstructure, as the initial permeability represents the mobility of magnetic domain wall in response to the small applied field [17].

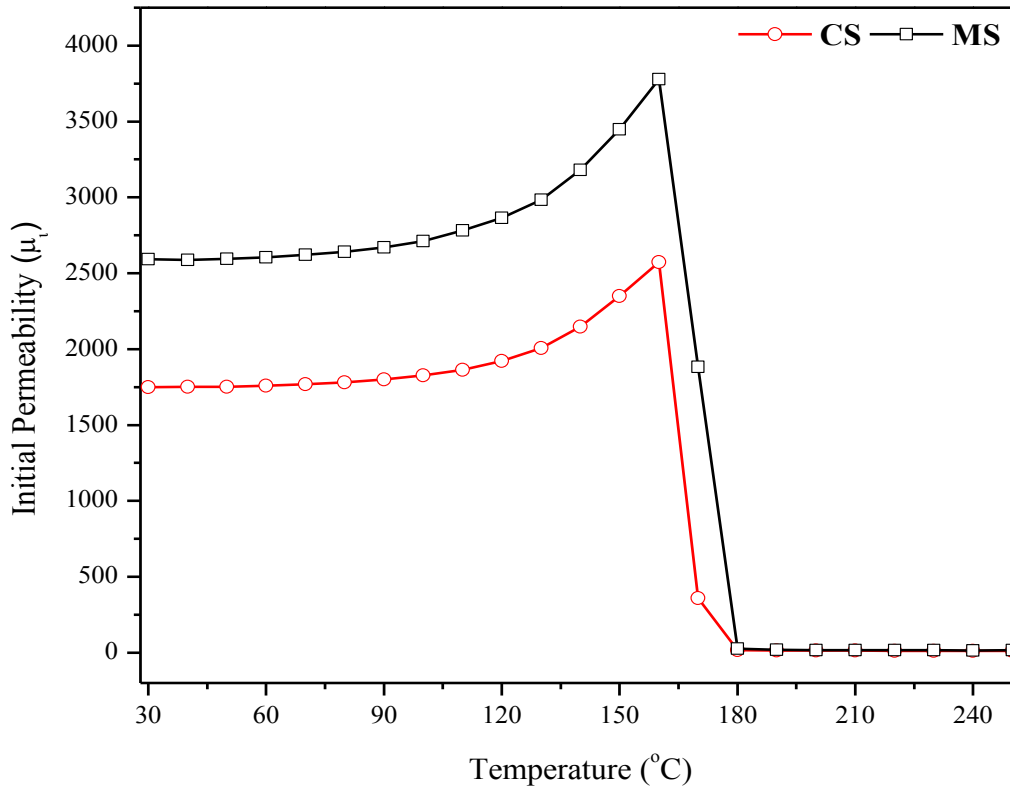


Fig. 4. Temperature dependence of magnetic permeability for Co-Cu-Zn ferrite samples prepared by CS and MS technique.

It is evinced from Fig. 2 that the microstructure becomes detrimental in permeability measurements. Obviously large-grain and dense samples can enhance permeability with domain wall displacement rather than the fine-grain ones having comparatively pores in between them. Pores in fact act as magnetic circuit breakers

Fig. 5 shows the magnetization versus external magnetic field (M–H curve) for the Co-Cu-Zn ferrite materials prepared by MS and CS routes.

For the CS material, the saturation magnetization (M_s) is 41.2 emu/g, while for MS sample, the M_s is 49.3 emu/g. It is clearly that the MS technique gives rise to larger M_s as compare with the CS technique, because the MS sample was completely crystallized and have bigger crystal grains (seen from Fig. 2).

The larger M_s is beneficial to minimize the devices size and decrease the loss. At the same time, larger H_c of the CS sample stems from the small crystal grains, which provides more pinning sites and grain boundaries.

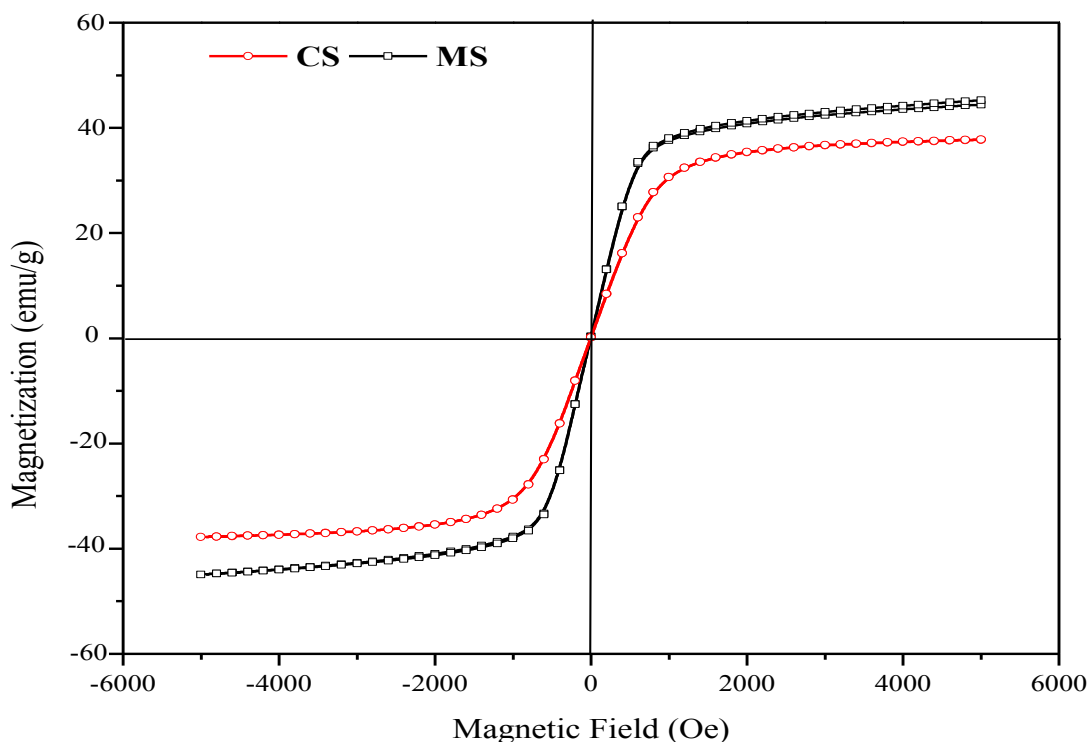


Fig. 5. M-H hysteresis loops for Co-Cu-Zn ferrite samples prepared by CS and MS techniques

4. CONCLUSION

In this paper, CoCuZn ferrite materials was prepared by two different routes (MS and CS) for a comparative study. The microstructure and electromagnetic properties were investigated and compared. The results show that the MS route material has excellent microstructure and good electromagnetic properties for applications in MLCI. Moreover, for MS technique the sintering temperature and time can be decreased from conventional 1250 °C to 900 °C and 2 h to 20 min, and the processing efficiency can also be improved significantly. The final conclusion is the microwave sintering (MS) process is a potentially important technique for synthesizing ferrites for their use in MLCI technology.

Acknowledgement

The author is thankful to UGC, New Delhi for providing her financial assistance to carry out this work. The author KKP is thankful to Prof. V. B. Helavi, Principal, Rajaram College and Prof P. R. Gaikwad, Director of Higher Education, Maharashtra state, Pune, India for their constant encouragement.

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(Received 17 September 2013; accepted 22 September 2013)