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Influence of sintering time on the structural, electrical and magnetic properties of polycrystalline $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites

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ABSTRACT

The effect of sintering time variation on grain size, density, porosity, dc electrical resistivity, activation energy, drift mobility, dielectric constant, loss factor, maximum magnetic flux density and coercivity of $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites has been reported. Grain size, density and drift mobility increased with the increase in sintering time. Porosity, dc electrical resistivity and activation energy decreased with the increase in sintering time. Dielectric constant decreased by increasing frequency for all the samples and it follows the Maxwell–Wagner's interfacial polarization. Loss factor was also studied. It has a decreasing trend followed by resonance peak with the rise of frequency.

1. Introduction

Properties of ferrites have been extensively investigated for the development of large variety of ferrites for their applications. Because of these benefits, the electrical properties of ferrites have become very important [1].

Naik and Power [2] have found a reduction in resistivity as well as in activation energy for Ni–Zn ferrites when sintered at high temperature. The observed decrease has been attributed to the reduced porosity and increased grain size at the higher sintering temperature. Jain et al. [3] have also quoted a similar decrease in dc resistivity in vanadium doped Ni–Zn ferrites with increase in sintering temperature.

Bera and Roy [4] found that apparent density and grain size increased whereas porosity decreased with the increase in sintering time of nickel–zinc ferrites.

Koops [5] performed experiments on a series of same composition with various sintering conditions and observed variation in resistivity and dielectric constant. These variations are attributed to the presence of Fe^{2+} concentration developed during sintering process. The variation in sintering parameters is much important in determining the electrical properties.

Sawant and Patil [6] investigated resistivity, dielectric constant and tan δ with the variation in frequency from 1 kHz to 50 MHz in $Cu_xZn_{1-x}Fe_2O_4$ ferrites. Resistivity and dielectric constant decrease with the increase in frequency whereas tan δ has peaks between 10^5 Hz and 10^6 Hz.

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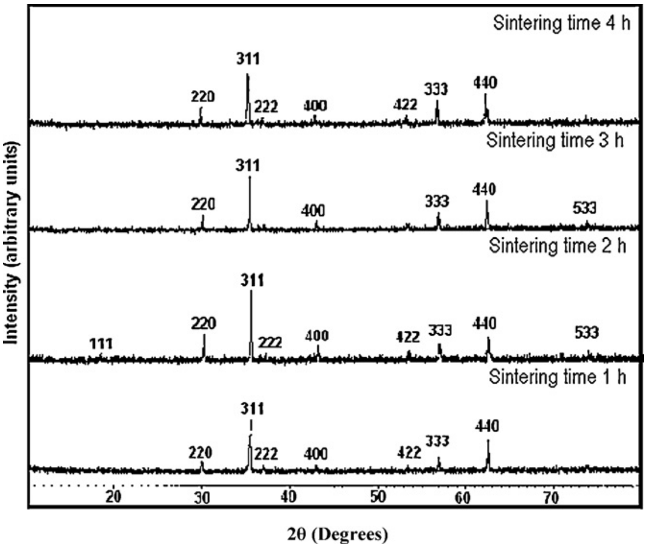


Fig. 1. XRD patterns for $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites.

Kulkarni and Patil [7] observed the existence of Yafet–Kittel (Y–K) type of magnetic ordering in $Zn_xCu_{1-x}Fe_2O_4$ ferrites which increases with the increase in zinc concentration. This was explained on the basis of three-sublattice model.

It is found that the composition $Cu_{0.6}Zn_{0.4}Fe_2O_4$ has comparatively less hysteresis losses. The purpose of this paper is to conduct a systematic study of Cu–Zn ferrites with the variation of sintering time.

In this paper, we report the preparation of $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites (sintering time = 1 h, 2 h, 3 h, 4 h) at 1100 °C by the standard solid state method. Consequent changes due to variation in sintering time with respect to above-mentioned properties have been discussed.

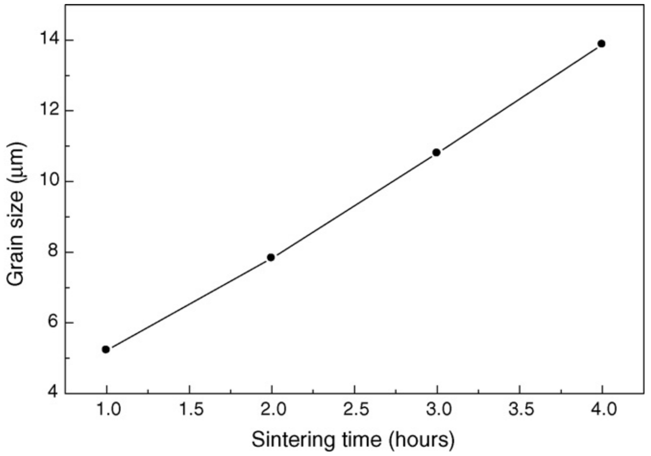


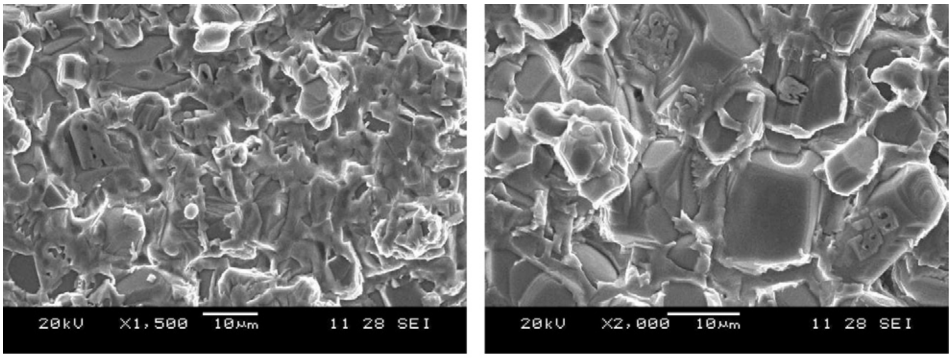
Fig. 3. Sintering time dependent grain size for $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites.

2. Experimental techniques

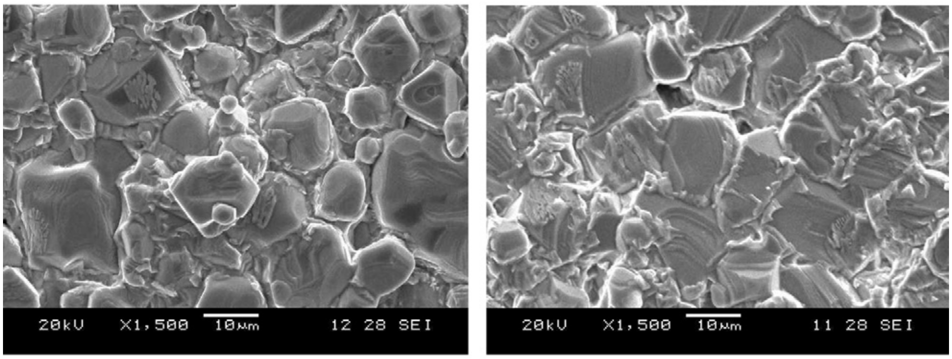
2.1. *Synthesis of $Cu_{0.6}Zn_{0.4}Fe_2O_4$ samples*

Samples of $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrite (sintering time = 1 h, 2 h, 3 h, 4 h) at 1100 °C have been prepared by the standard solid state reaction technique using reagents of analytical grade. The samples were prepared by mixing CuO (99.5%), ZnO (99%), and Fe_2O_3 (95%) in their respective stoichiometric ratio. Each sample with specific composition was ground in an agate mortar and pestle for 2 h. Before and after the grinding of each sample, the mortar and pestle were cleaned with acetone. Samples were calcined in the muffle furnace at 970 °C for 9 h followed by furnace cooling. Again each sample was ground in the agate mortar and pestle for 1 h. Then all the samples were pelletized with the help of polyvinyl binder by exerting uniaxial pressure of 100 kg/cm^2 for 1–2 min. Samples were sintered in the muffle furnace at a temperature of 1100 °C with the variation of sintering time followed by furnace cooling.

X-ray diffractions of the samples were carried out at room temperature using PAN-alytical diffractometer system with CuKα (λ = 1.5406 Å). The crystal structure was determined and lattice parameters '*a*' of the samples were calculated from the



1 hour 2 hour



3 hour 4 hour

Fig. 2. SEM of $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites with the variation of sintering time.

Table 1
Apparent density(ρ_a), resistivity (ρ), correlation coefficient (R) and activation energy (ΔE) of $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites.

	Sintering time (in hours)			
	1 h	2 h	3 h	4 h
ρ_a (g/cm^3)	4.510	4.565	4.599	4.626
ρ at 500 K × (10^4 Ω cm)	5.98	4.91	3.36	1.66
R	0.999	0.999	0.999	0.999
ΔE (eV)	4.707	4.676	4.638	4.596

data collected through XRD information. The apparent density ρ_a, X-ray density ρ_x, porosity P, resistivity ρ and drift mobility μ_d as a function of sintering time were also calculated.

As ferrites have very high resistivity so two-probe method was adopted to measure the electrical resistivity of the samples in the temperature range 300–520 K. Same specimen was used to measure the dielectric properties. Air-dried silver paint was applied on the flat surfaces to form electrodes for dielectric measurements. The capacitance C of the samples was measured using a WANE KERR 4275 LCR Meter Bridge in the frequency range of 80 Hz to 1 M Hz at room temperature from which the dielectric constant was calculated.

Magnetic properties were measured by a magnetometer, Rekien Denish. *B*–*H* loop measurements were performed on torrides with primary and secondary windings with enameled copper wire, using hysteresis loop tracer.

3. Results and discussion

Soft ferrite system $Cu_{0.6}Zn_{0.4}Fe_2O_4$ (sintering time = 1 h, 2 h, 3 h, 4 h) has been indexed using information from XRD patterns [8]. The indexed patterns shown in Fig. 1 confirmed the formation of single phase spinel structure. The micrographs of the mentioned materials are shown in Fig. 2.The grain size of the sintered materials was measured with the help of the computer attached with SEM. It increases from 5.22 μm to 13.88 μm with the increase in sintering time from 1 h to 4 h for the sintered materials as given in Fig. 3. It depends upon the sintering conditions, longer the sintering time greater will be the grain size due to the formation of larger amount of liquid phase in the system [4].

The apparent density was calculated using the relation:

$$\rho_a = \frac{m}{\pi r^2 h} \tag{1}$$

Here m is the mass, r is the radius and h is the width of the sample. It increases for these materials from 4.510 g/cm^3 to 4.626 g/cm^3 as the sintering time is increased from 1 h to 4 h as shown in Table 1.

The porosity of the samples was calculated from the relation:

$$P = 1 - \frac{\rho_a}{\rho_x} \tag{2}$$

It decreases from 0.159 to 0.134 as mentioned in Fig. 4. The rate of increase in density as well as the decrease in porosity seems to be higher at 1 h sintering than for 2–4 h sintering. The lower rate of densification above 1 h may be due to the higher amount of Zn-evaporation losses [4].

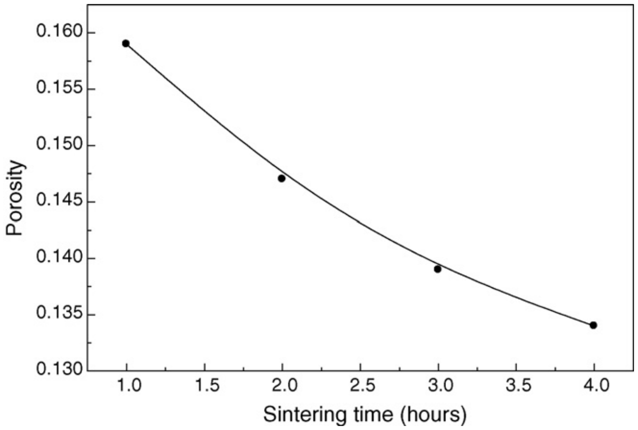


Fig. 4. Porosity vs sintering time for $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites.

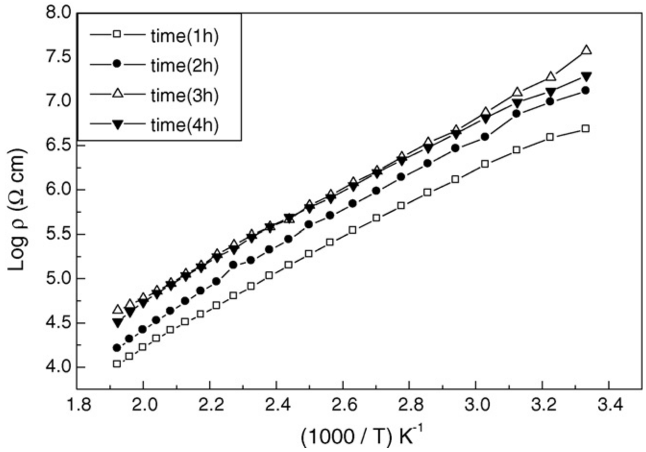


Fig. 5. Temperature dependent resistivity along with sintering time for $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites.

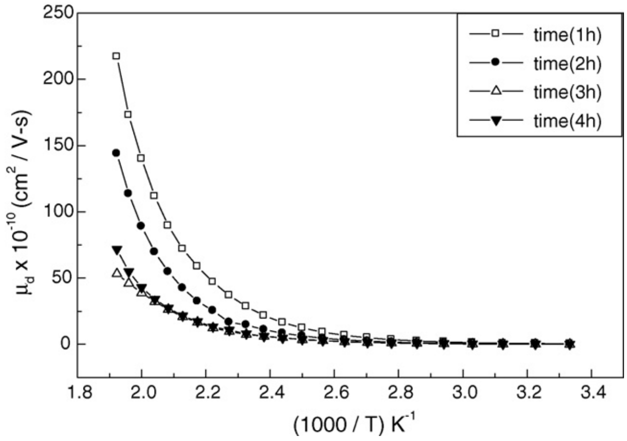


Fig. 6. Temperature dependent drift mobility along with sintering time for $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites.

The dc resistivity for all these samples was measured by two-probe method. The relationship between resistivity and temperature may be expressed as [9]:

$$\rho = \rho_\infty e^{\Delta E/k_B T} \tag{3}$$

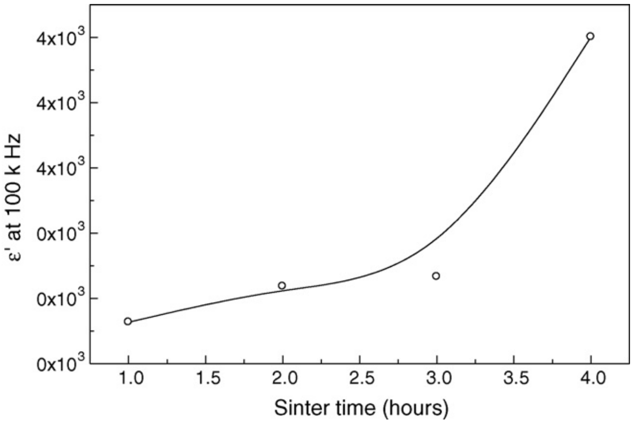


Fig. 7. Dielectric constant as a function of sintering time at 100 kHz of frequency for $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites

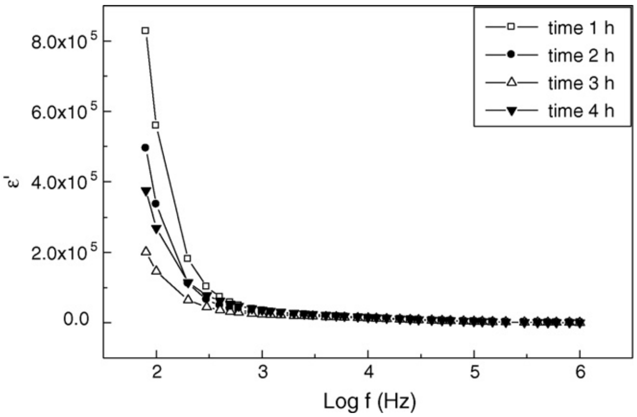


Fig. 8. Frequency dependence of dielectric constant along with sintering time for $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites.

Here ρ is the resistivity, T is the absolute temperature, k_B is the Boltzmann constant and ΔE is the activation energy.

The dc electrical resistivity of the sintered system was found to decrease from $5.98 \times 10^4\ \Omega$ cm to $1.66 \times 10^4\ \Omega$ cm at 500 K with the increase in sintering time from 1 h to 4 h as given in Table 1. Verwey and De Boer [10] reported that in oxides containing ions of a given element present in more than one valence state, conduction takes place by hopping of electrons between divalent and trivalent iron ions within the octahedral positions without causing a change in the energy state of the crystal as a result of transition. At higher sintering temperature, there are more divalent iron ions and more conduction which decreases the resistivity.

Temperature dependent dc resistivity measured in the temperature range of 300–520 K is given in Fig. 5. It follows the Arrhenius plot. This graph shows that by increasing temperature, the resistivity of $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites decreases. This is the property of semi-conductor in the sintered ferrites.

The activation energy of the sintered samples was found from the slope of the resistivity graphs. It decreases with the increase in sintering temperature. It is also due to the fact that materials having higher conductivity have low activation energy and vice versa.

Drift mobility (μ_d) of the samples have been calculated using the following relation [11]:

$$\mu_d = \frac{1}{\eta e \rho} \tag{4}$$

Here e is the charge on an electron, ρ is the resistivity at a particular temperature and η is the concentration of charge carriers that can be calculated from the relation [12]:

$$\eta = \frac{N_a \rho_a P_{Fe}}{M} \tag{5}$$

Here M is the molecular weight, N_a is the Avogadro number, ρ_a is the apparent density of the samples and P_{Fe} is the number of iron atoms in the chemical formula of the oxide.

There is increase in drift mobility from 46.11×10^{-10} to 161.87×10^{-10} (cm^2/V s) at 500 K with the increase in sintering time from 1 h to 4 h as given in Table 1. It can be seen that samples having low resistivity have higher mobility and vice versa [1]. To examine the temperature dependence of mobility a graph between mobility (μ_d) and $1000/T$ is shown in Fig. 6. It is observed from the graph that by increasing temperature, mobility increases. It may be due to the hopping of charge carriers from one site to another as the temperature increases [1].

Dielectric constant was calculated as:

$$\varepsilon' = \frac{Cd}{\varepsilon_o A} \tag{6}$$

where C is the capacitance of the pellet in farad, d is the thickness of the pellet in meters, A is the cross-sectional area of the flat surface of the pellet and ε_o is the constant of permittivity for free space.

The variation in dielectric constant with respect to various sintering conditions is shown in Fig. 7. Values of dielectric constant

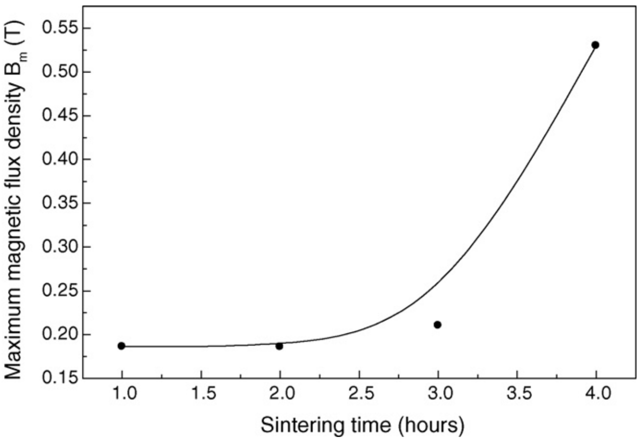


Fig. 10. Maximum magnetic flux density with the variation in sintering time for $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites

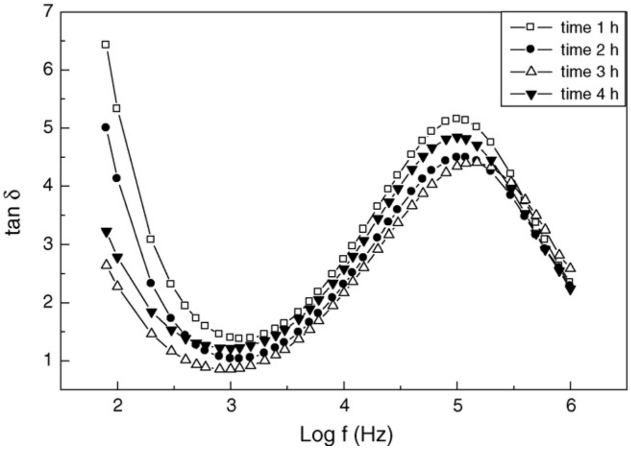


Fig. 9. Frequency dependence of loss factor along with sintering time for $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites

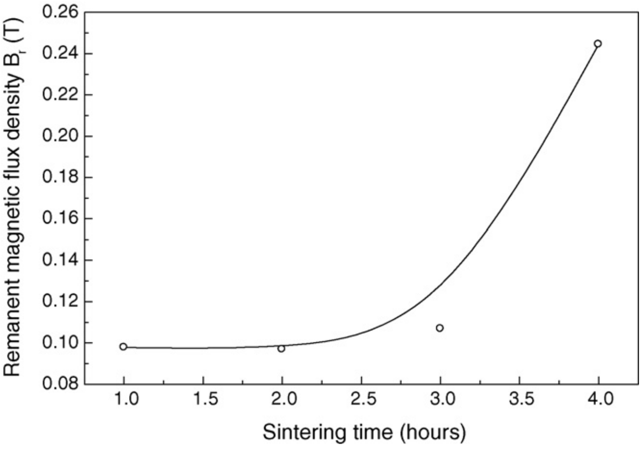


Fig. 11. Sintering time dependent remanent magnetic flux density for $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites.

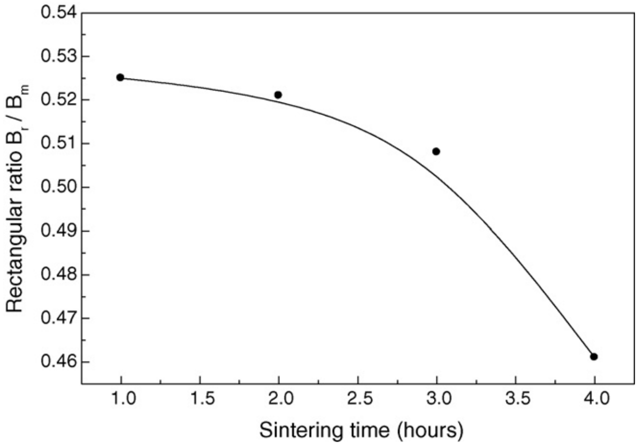


Fig. 12. Rectangular ratio vs sintering time for $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites.

are found to increase with increase in sintering time. The observed dielectric behavior can be explained on the basis of the assumption [13] that the mechanism of dielectric polarization to be similar to that of conduction. Electronic exchange between Fe^{2+} and Fe^{3+} is due to the local displacement of electrons in the direction of electric field which determines the polarization in ferrites. As discussed earlier, the increase in sintering time brings an increase in Fe^{2+} concentration and is responsible for the increase in polarization. Thus a comparatively high value of dielectric constant is expected for the sample sintered for longer time as the number of Fe^{2+} ions available for the polarization is large. Any decrease either in sintering temperature or in sintering time decreases the available Fe^{2+} ions and there is decrease in dielectric constant.

Variation of dielectric constant (ε') with frequency is shown in Fig. 8. Value of ε' is very high at lower frequencies. It decreases by increasing frequency. At very high frequency, it becomes independent of frequency. The variation in dielectric constant may be explained on space charge polarization which is produced due to the presence of higher conductivity phases (grains) in the insulating matrix (grain boundaries) of a dielectric produces localized accumulation of charge under an electric field [14]. As the assembly of space charge carriers in a dielectric takes a finite time to line up their axes parallel to an alternating electric field, if the frequency of the field reversal increases, a point is reached where the space charge carriers cannot keep up with the field and the alternation of their direction lags behind that of the field [14]. This results in the reduction of dielectric constant of the material. As the frequency of the field continue to increase, at some stage, the space charge carriers will start to move before the field reverses and make no contribution to the polarization of the dielectric. Shaikh et al. [15] have quoted a similar trend for dielectric constant with the change in frequency. According to Maxwell and Wagner two-layer model [16,17] space charge polarization is because of inhomogeneous dielectric structure of the material. It is formed by large well conducting grains separated by thin poorly conducting intermediate grain boundaries. Rabinkin and Novikova [13] pointed out that polarization in ferrites is a similar process to that of conduction. The electron exchange between $Fe^{2+} \leftrightarrow Fe^{3+}$ results the local displacement of electrons in the direction of applied field determines the polarization. Polarization decreases with the increase in frequency and ultimately reaches a constant value. It is due to the fact that beyond a certain frequency of external field, the electron exchange $Fe^{2+} \leftrightarrow Fe^{3+}$ cannot follow the alternating field.

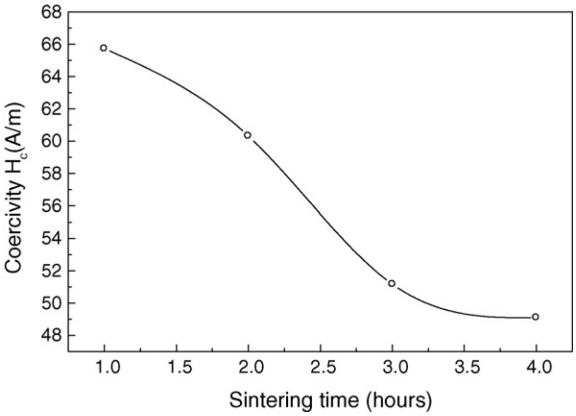


Fig. 13. Coercivity with the variation in sintering time for $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites.

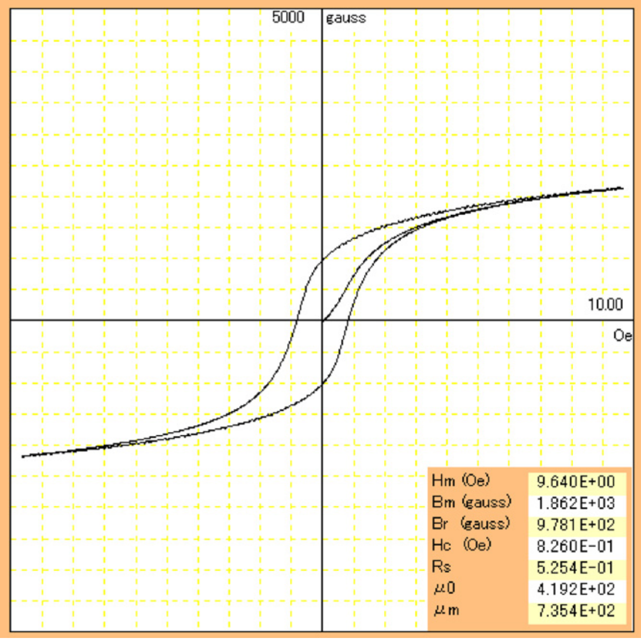


Fig. 14. *B–H* curve for $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites with sintering time 1 h.

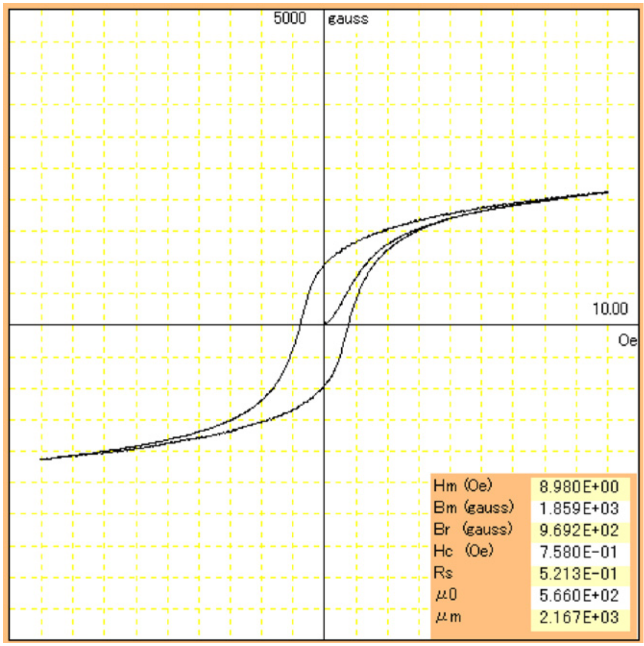


Fig. 15. *B–H* curve for $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites with sintering time 2 h.

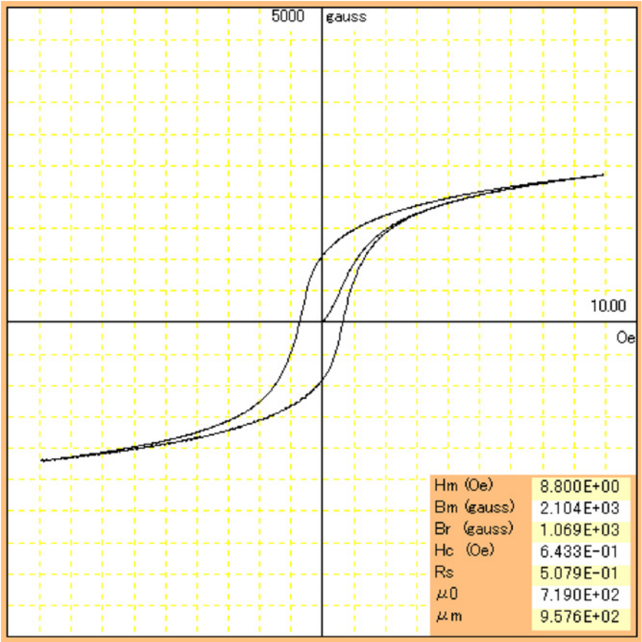


Fig. 16. *B–H* curve for $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites with sintering time 3 h.

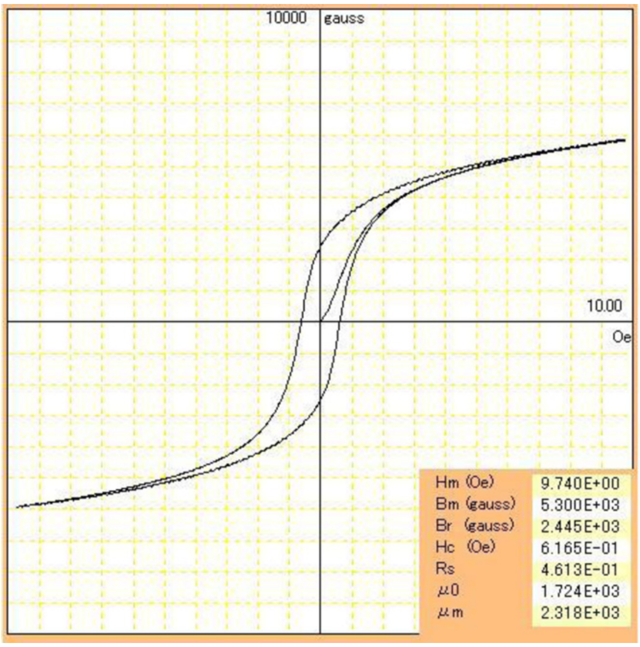


Fig. 17. *B–H* curve for $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites with sintering time 4 h.

Dielectric constant ε' has large values at lower frequency. It is because of the predominance of species like Fe^{2+} ions, oxygen vacancies, grain boundary defects, interfacial dislocation pile ups and voids [17,18]. The decreasing trend in ε' with the increase in frequency is natural due to the fact that any species contributing to polarizability is found to show lagging behind the applied field at higher frequencies [19].

Loss factor decreases from 6.424 to 0.852 with the increase in frequency from 80 Hz to 1 MHz as mentioned in Fig. 9. Values of $\tan\delta$ depend on a number of factors such as stoichiometry, Fe^{2+} content and structural homogeneity, which in turn depends on the composition and sintering time of the samples [20]. In our measured range of frequency, all the samples have peaks. The peaking nature occurs when the jump frequency of the electrons between Fe^{2+} and Fe^{3+} is equal to the frequency of the applied field.

Resonance peak appearance can be explained as follows. If an ion has two equilibrium positions A and B of equal potential energies separated by a potential barrier. The ion has same probability of jumping from A to B and from B to A. The frequency with which the ion exchanges its position between these two states is called the natural frequency of jump between these two states. When an external alternating electric field of natural frequency is applied, maximum electrical energy is transferred to the oscillating ions and power loss increases highly, resulting in resonance. Therefore peaks appear [21].

3.1. Magnetic properties

The results of hysteresis measurements such as maximum magnetic flux density B_m, remanent magnetic flux density B_r, coercive force H_c and B_r/B_m of $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites for different sintering time are given in Figs. 10–13. The alternating current in the primary coil of torroidal rings for all the samples was kept constant for obtaining the *B–H* loops. A decrease in H_c and the ratio B_r/B_m with the increase in sintering time is observed as quoted by Verma et al. [20]. This decrease in H_c may be attributed to an increase in grain size and decrease in porosity of the samples. Grain size increases with the increase in sintering time. Bigger grains have more number of grain walls. The magnetization/demagnetization due to domain wall movement requires less energy as compared to energy required for domain rotation. As the number of walls increases with grain size, the contribution to magnetization or demagnetization due to wall movement than that due to domain rotation increases. Therefore, the samples having bigger grains are expected to have low coercivity. The decrease in B_r/B_m shows that the *B–H* loop deviates from rectangularity with the increase in sintering time (Figs. 14–17).

4. Conclusion

Variation of sintering time of $Cu_{0.6}Zn_{0.4}Fe_2O_4$ ferrites causes appreciable changes in its structural, electrical and magnetic properties. Grain size, apparent density and drift mobility increase with the increase in sintering time. Porosity, dc electrical resistivity and activation energy decrease with the increase in sintering time. Dielectric constant increases with the rise in sintering time. The dielectric constant and dielectric loss factor both decreases with the increase in frequency. This decrease has been explained on the basis of space charge polarization resulting from the electron displacement. Coercivity and the ratio of remanent magnetic flux density to maximum magnetic flux density decrease with the increase in sintering time.

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