

Processing of Nano-crystallite Spinel Ferrite Prepared by Co-precipitation Method

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Abstract

Active powder of Cu substituted Mn-Zn ferrite was synthesized by soft chemical approach called co-precipitation method. The initial permeability, density, grain size, curie temperature and dc resistivity have been studied. X-ray diffraction (XRD) method confirmed the sample to be a single-phase spinel and consists of nano-structure (~35nm). Further, scanning electron micrograph (SEM) also confirmed nano-phase and the uniformity of the particles. The initial permeability values do not exhibit much variation with temperature, except near curie temperature, where it falls sharply. The initial permeability is found to increase with the increase in sintering temperature. This is attributed to the increase in the grain size.

Keywords: Co-precipitation; X-ray Diffraction; Scanning Electron Micrograph; Initial Permeability.

Introduction

Soft ferrites are most versatile because of their many technological applications [1-8]. Recently, multilayer chip ferrite inductor (MLCI) has been rapidly developed as an important surface mounting device for electronic applications.

To achieve reliable performance of multilayer device, the ferrite powder needs to be sintered at <900° C. Ni-Cu-Zn ferrite is usually used as magnetic material for MLCIs because of its good properties at high frequencies and low sintering temperatures [9-10].

Mn-Cu-Zn ferrite has similar magnetic properties to those of Ni-Cu-Zn ferrite with the advantage that they are economical [11] and easy to synthesize. Therefore, Mn-Cu-Zn ferrite will be a potential candidate material for multilayer chip inductor with high performance and low cost.

Experimental details

Cu substituted Mn-Zn ferrite of composition $\text{Mn}_{0.4}\text{Cu}_{0.2}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ was prepared by co-precipitation method. The materials used were manganese chloride (98% Merck, India), copper chloride (96% Merck, India), zinc chloride (96% Merck, India), iron (III) chloride (98% Merck, India) and sodium hydroxide (96% Merck, India). One molar solution of these materials was made with distilled water. 70ml sodium hydroxide was taken from one molar solution in approximately 1760 ml of distilled water to have the concentration of 0.37mol/litre and heated to boiling. Manganese chloride, copper chloride, zinc chloride and iron (III) chloride were taken from their molar solution in accurate stoichiometric proportions.

These solutions were poured as quickly as possible into boiling solution of NaOH under vigorous stirring produced by the glass mechanical stirrer (~ 500 r.p.m.). Mixing is very important; otherwise segregation of phases can take place. After co-precipitation, pH is set 12.5-13. Reaction vessel is covered with plastic cover to diminish evaporation of the solution. Reaction is continued for 30-40 minutes at temperature 90-100°C under vigorous stirring. Reaction vessel is cooled to ambient temperature and particles precipitate. Total volume is reduced to ~500ml by aspiration of supernatant. Suspension is centrifuged in 4 beakers at 7000 r.p.m. for 10 minutes. Precipitate is washed with distilled water of ~900ml and centrifuged once more in 4 beakers at 7000 r.p.m. for 10 minutes.

The residue is dried and was calcinated in a box type furnace at 200°C for 15 hours at the rate of 200°C /h to obtain a ferrite powder. This powder was mixed with 2% P.V.A. binder and pressed into pellets of 1.50cm diameter and 0.20 mm thickness under pressure of 5 tons (1 ton = 1.016×10^3 kg) and rings of 1.5 cm outer diameter, 1.0 cm inner diameter and 0.20 cm thickness under a pressure of 3 tons. These samples were sintered in air at 700°C and 800°C at a heating rate of 250°C /h for 2 hour and were subsequently cooled. The pellets were coated with silver paste to provide electrical contacts and the rings were wound with about 50 turns of 30 SWG enameled copper wire to form torroids. X-ray diffraction (XRD) measurements were taken on a Rigaku Geiger Flex 3 kW diffractometer using CuK_α source. Scanning electron micrograph (SEM) was recorded using Cambridge Stereo Scan 360 scanning electron micrograph. The initial permeability was measured by using Agilent Technologies 4285A Precision LCR Meter. Resistivity was measured by using Two-Probe method. Curie temperature was measured by using gravity method.

Result and Discussion

X-ray diffraction patterns of the sample $\text{Mn}_{0.4}\text{Cu}_{0.2}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ sintered at 700°C and 800°C for 2 hour were studied and shown in figure 1. The observed diffraction lines were found to correspond to those of the standard pattern of Manganese ferrite [8] with no extra lines, indicating thereby that the samples have a single-phase spinel structure and no unreacted constituents were present in these samples. Lattice constant 'a' for the samples sintered at 700°C and 800°C were calculated from the observed 'd' values and found to be 8.328°A and 8.339°A respectively. The peak becomes sharper with the increase in sintering temperature. The particle size of the samples has

been estimated from the broadening of the X-ray diffraction peaks using the Scherrer equation [12] for Lorentzian peak

$$d = \frac{0.9 \lambda}{(w - w_1) \cos \theta}$$

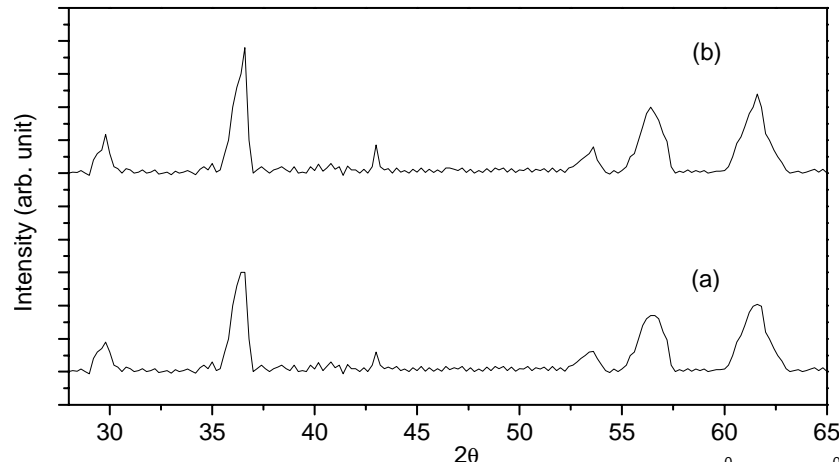


Figure 1: XRD pattern for $Mn_{0a} Cu_{02} Zn_{0a} Fe_2 O_a$ ferrite sintered at (a) $700^\circ C$ (b) $800^\circ C$

where, d is the grain diameter, w and w_1 are the half intensity width of the relevant diffraction peak and the instrumental broadening respectively, λ is the X-ray wavelength and θ is the angle of diffraction. The particle size was found to be 56 nm at $700^\circ C$ and 65 nm at $800^\circ C$. This indicates that the crystal phase was transformed from cubic spinel structure in the synthesized powder into the tetragonal one after sintering. In fact, Mn-Zn ferrite is cubic spinel and $CuFe_2O_4$ is tetragonal at $<760^\circ C$ [13]. Hence, Mn-Cu-Zn ferrite should have a tetragonal distorted structure due to Cu incorporation into ferrite lattice. This tetragonal distortion, however, was not noticed in the synthesized nano-sized powder at $700^\circ C$. This may be attributed to the fact that at low temperature the cations are statistically distributed in the ferrite lattice formed. During sintering, the redistribution of cations occurs to form an ordered structure. The disordered nano-sized particles can be expected to possess high sintering reactivity.

Fig.2 shows the SEM microphotograph of the Mn-Cu-Zn ferrite sintered at $700^\circ C$. It is clearly seen that the ferrite is composed of uniform nano-particles. Hence, densified ferrite with a fine-grained microstructure behaviour can be prepared at $<950^\circ C$ by using precipitation-derived nano-crystalline powder. The average grain size is found in accordance with above calculated results. The Mn-Cu-Zn ferrite powder with the same composition, synthesized by the conventional solid-state reaction method, can be sintered only at temperatures above $1050^\circ C$ [14]. Bhosale et.al. [15] reduced the sintering temperature to $1050^\circ C$ by using a fine powder synthesized through the oxalate precursor method. So, the synthesized nano-sized powder exhibits highly reactive behaviour and can be sintered at $950^\circ C$ without any

low-melting-point additives. This is of importance for the high-performance MLCIs, because the low-melting-additives in low-temperature sintered ferrites are usually detrimental to the reliability of MLCIs. The high activity of the synthesized powder may originate from the nanometer scale particle size and disordered crystal structure.

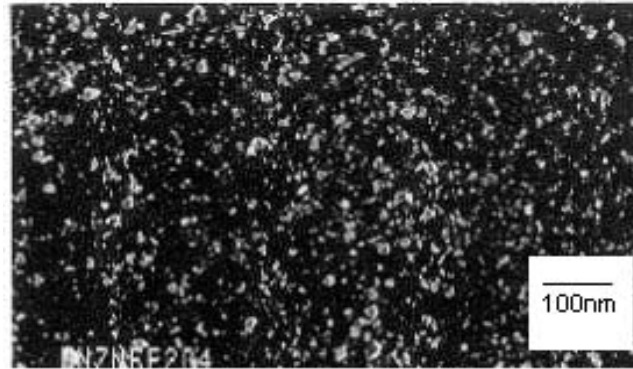


Figure 2: Scanning electron micrograph of fractured surface of Mn-Cu-Zn sintered at 700^o C .

The electromagnetic properties, initial permeability and electrical resistivity, were measured on the torroids and pellets. Table 1 summarizes the density, average grain size, initial permeability, curie temperature, specific temperature coefficient and electrical resistivity of ferrites sintered at 700^oC and 800^oC. The specific temperature coefficient of permeability, α_T , was calculated from the following relation,

$$\alpha_T = (\mu_{T_2} - \mu_{T_1}) / \mu_i \mu_i (T_2 - T_1)$$

where, μ_{T_2} and μ_{T_1} are the permeability at temperatures T_2 and T_1 (here, $T_1 = -25^\circ\text{C}$ and $T_2 = 100^\circ\text{C}$) respectively, μ_i is the permeability at 25^oC. It can be noticed from Table 1 that Mn-Cu-Zn ferrite possesses good electromagnetic properties, similar to those of the low-temperature sintered NiCuZn ferrites. All electromagnetic properties fulfill the requirements of MLCI. Therefore, the synthesized Mn-Zn-Cu ferrite can be used as a magnetic material for MLCIs.

Table 1: Density, average grain size and the main electromagnetic properties for Mn-Cu-Zn ferrites sintered at 700^o C and 800^oC.

Sintering Temperature (°C)	Density (g/cm ³)	Grain Size (nm)	μ_i @ 100kHz	T_c (°C) from fig.3	T_c (°C) experimental	α_T (x10 ⁻⁶ /°C)	ρ x10 ⁷ (Ω.cm)
700	4.94	56	356	205	207	7.4	3.7
800	4.95	65	518	204	205	7.3	2.5

The initial permeability of low-temperature sintered Mn-Cu-Zn ferrite as a function of temperature is shown in Fig.3. In the temperature range -25 to 205°C, there is a small permeability variation, which makes this material suitable for MLCI application. The sharp drop of the permeability at the Curie point indicates a good homogeneity in composition for the ferrite prepared by the co-precipitation method.

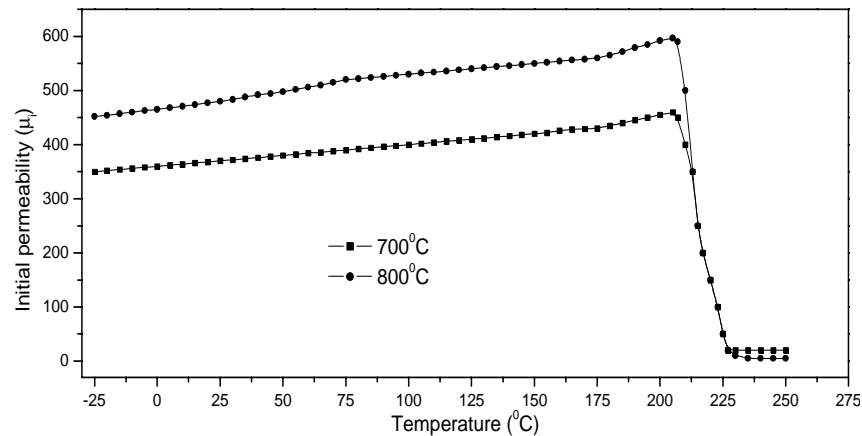


Figure 3: Initial permeability of low temperature sintered Mn-Cu-Zn ferrites as a function of temperature

Curie temperature as seen from fig. 3 is in accordance with experimental values (Table 1). In addition, the permeability of Mn-Cu-Zn ferrite increases with the increasing sintering temperature. This is attributed to the increase in grain size. A plateau is also noticed in the permeability-temperature curve of the sample sintered at 900°C. This indicates that the shape of the permeability-temperature curve depends on the preparation conditions.

Conclusion

We can conclude that the co-precipitation method is an effective and convenient route to synthesize nano-crystalline Mn-Cu-Zn ferrite particles because there is no requirement for a calcination process at high temperature. The synthesized powder has high activity due to its nano-sized particle size and disordered structure. The ferrite powder can be sintered at <950°C, and possesses a fine-grained microstructure. The low-temperature sintered Mn-Cu-Zn ferrite has good electromagnetic properties, which makes this material suitable for MLCI application.

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