

DC resistivity of Cu substituted Ni-Zn ferrites processed through Standard Ceramic

Method

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ABSTRACT

Cu substituted Ni-Zn ferrites are processed through standard ceramic method to make use of them for multilayered chip inductor applications. X-ray diffraction and dc resistivity were carried out on these samples. Cu ions entered into the lattice and formed liquid phase at the grain boundaries of the ferrite material. Activation energies of these ferrites also examined and observed to following electron hopping mechanism.

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Introduction:

The chip inductor is fabricated by laminating ferrite layers and internal metallic conductors alternately and then co-firing to form the monolithic structure [1]. In general, Ag, Pd metal or Ag/Pd alloy are used as an internal conductor. Ag is preferred among them due to its low cost, oxidative resistibility and low electrical resistivity resulting in components with high quality factor. Since the melting temperature of Ag is 961°C, the ferrite ceramics are required to be sintered at temperatures below 950°C to prevent Ag diffusion into the ferrite that would damage the insulation resistivity of ferrite [2-6].

Presently, NiCuZn ferrites have been the dominant materials for MLCI due to its low sintering temperature (<950°C) and good electromagnetic properties [7, 8]. In addition, NiCuZn ferrites have better high frequency properties compared to that of MnZn ferrite and low densification temperatures than NiZn ferrites [7, 9]. Several studies have been conducted to enhance the properties of NiCuZn ferrite. Important approaches adopted are: (a) the reduction of the particle size to improve densification, (b) using sintering aids for better densification and (c) substitutions at tetrahedral and octahedral crystallographic site in the spinel ferrite to improve electrical and magnetic properties.

Cu is conventionally used in NiCuZn ferrite to improve densification as well as electromagnetic properties [10]. The beneficial effect of copper ions on the densification of ferrite can be reasonably explained by possible sintering mechanisms that take place through a high atomic mobility of Cu ions at relatively

low temperature. The increase of the lattice diffusion usually increases the diffusion path leading to an increase of the rate of cation inter diffusion in the solid solution, which is in agreement with the lattice diffusion mechanism proposed by Gupta and Coble [11, 12]. During sintering grain boundary diffusion [13] may play an important role in the grain growth because the activation energy for lattice diffusion is higher than that for grain boundary.

To obtain materials with high permeability as well as high Q , a key step is to tailor the additives composition to produce densification with limited grain growth. During the grain growth, the dissolution of the additive into the ceramic is assisted by solution re-precipitation process, which reduces the volume fraction of intergranular phases. Therefore, Cu has been selected as a substituent in Ni-Zn ferrite in the current investigation. Cu is used in this ferrite to decrease the sintering temperature. However, Cu decreases the resistivity of the ferrite, which is not desirable for its high frequency applications. So, optimization of Cu content with respect to densification and resistivity of the ferrite is very important.

Experimental details:

The NiCuZn ferrites were prepared by the solid-state reaction method. Analytical grade NiO, ZnO, CuO and Fe₂O₃ were weighed in the following compositions Ni_{0.7-x}Cu_xZn_{0.3}Fe₂O₃, with x=0.00-0.40 and then mixed for 6 hours using agate mortar. The mixed powders was followed by calcining at 850°C for four hours. After grinding the calcined powder 5 wt% of polyvinyl alcohol

binder (PVA) was added to the dried powder and granulated. The granulated powder was pressed at a pressure 2000 kg cm⁻¹ to form pellets. The specimens sintered at 1100°C for 4 hours in air atmosphere.

The density of the sintered specimens was measured by Archimede’s method. The ferrite phase was identified by X-ray diffraction using Cu-K α radition. The DC resistivity at room temperature was measured by Hewlett Packard 4140 LCR meter.

Results & Discussion:

The phase formation behavior was studied by XRD. Fig. shows the XRD patterns of the as-burnt ferrite powders. Miller indices (h k l) are represented for each peak in the X-ray diffraction patterns. The powders were in crystalline state and identification revealed spinel ferrite phases similar to JCPDS card number 48-0489. Accurate determination of lattice constant has been obtained from the extrapolation of calculated lattice constant against Nelson-Riley function [14] for which the function is zero. Lattice constant for the set of compositions is given in table 1.

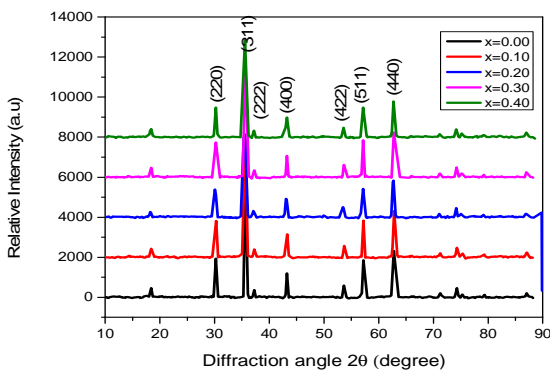


Table 1: Lattice constant versus Cu concentration

X	Lattice constant (Å ^o)
0.00	8.37
0.10	8.39
0.20	8.40
0.30	8.41
0.40	8.43

Lattice parameter was found to increase with increasing Cu substitution. In general, in Ni-Zn ferrites, Zn ions tend to occupy A-sites and Ni ions have preference for B-sites. When Cu ions replace Ni ions in B-sites, a slight increase in the lattice constant is expected because of the larger ionic radius of copper (0.79 Å) compared to the Ni²⁺ (0.74Å) [15]. It is well known that replacement of a large ion by a small ion eventually increases the lattice constant of the ferrite lattice and the same has been noticed in the current investigation.

Ferrites structurally form cubic close-packed oxygen lattices with the metal ions at tetrahedral (A) and octahedral [B] sites. In general, the conduction mechanism in ferrites can be explained by the Verwey electron hopping model [16] which

involves exchange of electrons between ions of the same element in different valence states, and are distributed randomly over crystallographically equivalent lattice sites. The conduction is due to the exchange of 3d electrons between Fe²⁺ and Fe³⁺ ions in the octahedral site. The formation of Fe²⁺ ions in tetrahedral site can be ruled out for the simple reason due to the absence of Fe²⁺ ions at A-sites and any Fe²⁺ ions formed during processing preferentially occupy B sites only. The formation of Fe²⁺ ions in the material is to satisfy the charge balance in the lattice. Creation of Fe²⁺ ions gives raise the transfer of electron between the Fe³⁺ and Fe²⁺ ionic states.

The variation in resistivity has been interpreted in terms of the contributions arise from (1) the presence of more number of grains and grain boundaries (2) the disappearance of pores and cracks with increasing annealing temperature and (3) the loss of zinc at elevated temperatures. The loss of zinc leads to the formation of ferrous ions in the lattice and thereby increases the conductivity.

In the present study, as the samples are sintered at 1100°C, loss of zinc from the material is expected which further creates pores in the material. Because of these pores, dc resistivity of the material increases. But copper act as a sintering aid and copper forms liquid phase at the grain boundary hence substitution copper leads to an increase in conductivity through grains in the material. Therefore a decrease in resistivity has to be observed with increasing Cu concentration. Similar tendency has been noticed in the current study.

As expected in semiconductors, the observed dc resistivity falls exponentially with increasing temperature for all these compositions. Activation energies for all the samples have been determined from the slope of log of resistivity (log ρ) versus reciprocal of absolute temperature (1/T) plots and are given in table 2. In general, in ferrites, the activation energy is decided by the hopping probability of electrons among Fe³⁺ ↔ Fe²⁺. Activation energies showed a similar tendency that of compositional dependency of dc resistivity of the material. Activation energies are in the range of 1.4 eV to 3 eV which represents hopping between the electrons among Fe³⁺ ↔ Fe²⁺.

Table 2: Activation energy versus Cu concentration

X	Activation Energy (eV)
0.00	0.28
0.10	0.18
0.20	0.23
0.30	0.14
0.40	0.21

Conclusions: X-ray diffraction studies indicate that copper ions occupied B-sites in the ferrite lattice and the decrease in dc resistivity also provides further information that copper ions form liquid phase at the grain boundaries. Activation energies of the ferrites suggest electron hopping in the material.

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