Available online at www.sciencedirect.com
SCIENCE DIRECT
ELSEVIER
Journal of Magnetism and Magnetic Materials 305 (2006) 110–119
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

Magnetic properties of NiCuZn ferrites synthesized by oxalate precursor method

S.A. Ghodake[a], U.R. Ghodake[a], S.R. Sawant[b], S.S. Suryavanshi[a,*], P.P. Bakare[c]

[a]*Department of Physics, Applied Electronics, Solapur University, Kegaon, Solapur 413 255, India*
[b]*Department of Electronics, Shivaji University, Kolhapur 416 004, India*
[c]*Centre for Material Characterization, National Chemical Laboratory, Pune 411008, India*

Received 13 December 2004; received in revised form 16 November 2005
Available online 8 February 2006

Abstract

Ni–Cu–Zn ferrites have been synthesized by employing co-precipitation technique using oxalate precursors. X-ray diffractograms did not show impurity phases, indicating single-phase formation of the ferrites. The diffractograms of oxalate complex decomposed at 650 °C show that ferritization is complete up to 650 °C. Lattice parameter a (Å) was found to decrease with the addition of Ni^{2+} which is attributed to ionic sizes of Ni^{2+} (0.69 Å), which replaces Cu^{2+} (0.72 Å). From the thermogravimetric studies it is observed that the experimentally observed total mass loss (%), agrees with theoretically calculated mass loss (%) indicating maintenance of requisite stoichiometry. Initial permeability (μ_i) shows increase when Ni^{2+} is added up to $x = 0.15$ while for ($x > 0.15$), it decreases. The increase in initial permeability (μ_i) is attributed to monotonic increase in Ms, and K_1 on addition of Ni^{2+}. However, the microstructure and density (porosity) also influence μ_i variations. The decrease in μ_i is attributable to increase of K_1. The composition with density 91.14% exhibits large μ_i which also tends to increase with temperature up to 60 °C. Thus its usable range extends up to 60 °C. This samples has T_c near to 160 °C.

Keywords: XRD; Magneticproperties; Magnetization; Initial permeability; NiCuZn ferrites

1. Introduction

Polycrystalline ferrites have been extensively used in many electronic devices, because of their high permeability in the radio frequency (RF) region, high electrical resistivity, mechanical hardness, and chemical stability. There has been a growing interest in Ni–Cu–Zn ferrites for the applications in producing multilayer type chips mainly because these oxides can be sintered at relatively low temperature with a range of compositions.

The quest for ceramic materials with high density, high purity, and high permeability has led to the investigation and evaluations of various unconventional preparative methods. Precursors are advantageous because they ensure excellent stoichiometry, low trace impurity content and maximum homogeneity [1–5]. For chemical synthesis, a precursor compound with intended stoichiometry is prepared first, which is decomposed at temperatures (<873 K) in a subsequent calcinations reaction to obtain the required metal oxides [6]. The oxalate precursors are usually preferred due to their low solubility, low decomposition temperature, and very fine particle nature [7].

Ideally, in order to achieve a complete reaction within the shortest time and at the lowest possible temperatures, mixing of component cations on an atomic scale is necessary. Compound precursors achieve this goal, but the stoichiometry of the precursors does not often strictly, coincide with the stoichiometry of the desired product [8]. Various authors [9,10] have investigated co-precipitation of metal oxalates from appropriately composed solutions in order to produce precursor compounds for spinel ferrites MFe_2O_4. Wickham [11] has synthesized spinel ferrites MFe_2O_4 (where $M = Mg^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, CO^{2+}$) in air at 873 K. Schroder [12] concluded that decomposition of mixed oxalates is an apparently low-temperature

*Corresponding author.
E-mail address: sssuryavanshi@rediffmail.com (S.S. Suryavanshi).

0304-8853/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jmmm.2005.11.041

phenomenon. Wang et al. [13] have synthesized NiCuZn ferrites by a ceramic method.

Zhang et al. [14] have synthesized NiCuZn ferrites by gel self-propagation method. They obtained ultra-fine and highly reactive NiCuZn ferrite powder by gel self-propagating method and concluded that densification of ferrites and homogeneous grain growth were the main factors affecting high initial permeability. In the present paper, we report the synthesis of NiCuZn ferrites by oxalate precursor method. The method is advantageous in obtaining homogenous solid solutions of oxalates, which on further decomposition yield the required ferrite compositions. Chemical analysis of ferrite compositions has been carried out by thermogravimetry. Thermal analysis has been carried out for determination of ferritization temperatures by simultaneous recording of thermogravimetry (TG)/differential thermogravimetry (DTG)/differential thermal analysis (DTA) plots (simultaneous thermal analysis STA) and also to confirm the experimental results of the thermogravimetry. X-ray diffraction (XRD) studies have been carried out to characterize the single spinel phase. Initial permeability, and magnetization studies have also been reported.

2. Experimental procedure

2.1. Synthesis

The oxalates were prepared by a method suggested by Wickham [15] and subsequently modified by Bremer et al. [16] for the preparation of manganese zinc ferrites.

Iron acetate was prepared by adding glacial acetic acid to the required quantity of AR grade iron metal powder to make a solution with a slight excess of glacial acetic acid and heating it in a CO_2 atmosphere instead of in a N_2 atmosphere as employed by earlier workers [16]. Required quantities of nickel acetate, zinc acetate, copper acetate and the above synthesized iron acetate (total metal ion concentration = 0.45 M) were slowly added to oxalic acid solution (0.60 M) to precipitate the required oxalate to maintain the desired stoichiometry. In this way, different oxalate complexes of the general composition $Ni_xCu_{[(1-t)-x]}Zn_tFe_2(C_2O_4)\cdot nH_2O$ (where $t = 0.45$, 0.50, 0.55, 0.60 and $x = 0.00$, 0.05, 0.10, 0.15, 0.20,0.30,0.40, 0.50, and 0.55) were synthesized.

2.1.1. Thermogravimetric (TG) studies

TG studies of oxalate complexes were carried out in the temperature range of room temperature to 700 °C. The percentage of weight loss of samples before and after heating was calculated from the experimental data.

2.1.2. X-ray diffractograms (XRD)

The co- precipitated oxalates were decomposed in the air at 650 °C for 1 h. XRD patterns (Fig. 1) of this powder material were recorded, by a Phillips X-ray Diffractometer model PW-1710, using CuK$\propto$ radiation and then analyzed. The XRD patterns revealed a single spinel structure and indicated the absence of any other impurity phase. To study μ_i, the powder obtained was compacted at 1.07×10^9 dyn/cm^2 for 1 min. into toroid form (outer diameter = 2 cm, inner diameter = 1 cm). The toroids were finally sintered at 1000 °C for 4 h. The rate of heating was 100 °C/h and the rate of cooling was 60 °C/h.

2.1.3. Saturation magnetization measurements (Ms) and initial permeability (μ_i)

Saturation magnetization was measured by the vibrating sample magnetometer (VSM) technique EG and G Princeton Applied Research Corporation (PARC) VSM model 4500. Initial permeability measurements of samples were carried out using HP-4284 A precision LCR meter in the range from room temperature to 450 °C at 1 KHz from low field inductance measurements of coils with toroidal cores using formula

$$\mu_i = L/(0.0046N^2 h \log d_2/d_1) \quad (1)$$

where L is the inductance in μH, N the number of turns, d_2 the outer diameter, d_1 the inner diameter, h the height of core in cm, and μ_i the initial permeability in μH/cm.

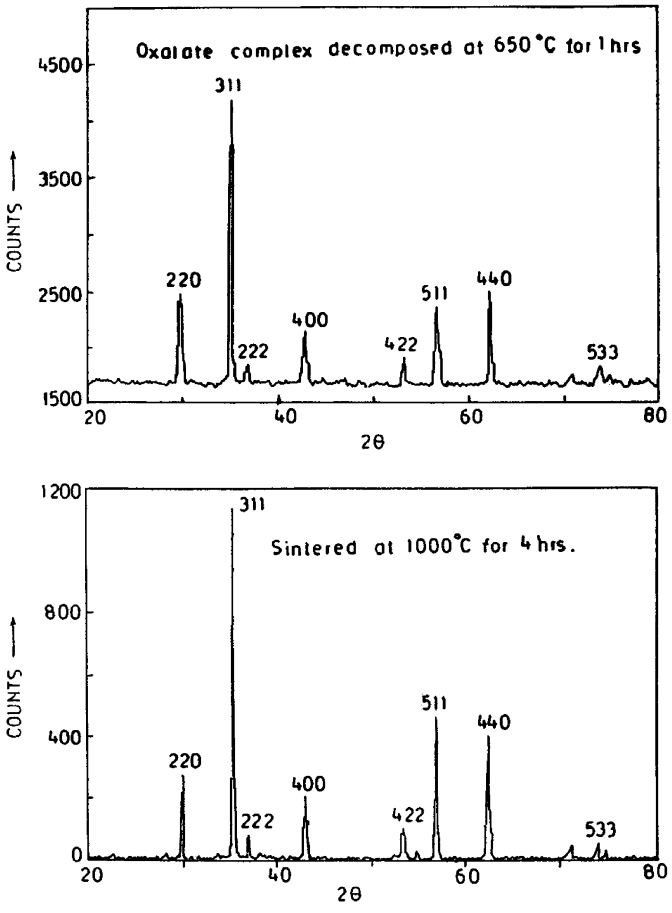

Fig. 1. XRD pattern for $Ni_{0.15}Cu_{0.30}Zn_{0.55}Fe_2O_4$.