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Analysis of the complex permeability of NiCuZn ferrites up to 1 GHz with regard to Cu content and sintering temperature

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Abstract

We have studied the frequency dependent permeability of $Ni_{0.60-x}Cu_xZn_{0.40}Fe_{1.98}O_4$ ferrites ($x=0$, 0.10, 0.20, 0.30) with regard to the Cu concentration and the undergone heat treatment. To this end, single-phase magnetic ceramics were prepared and characterized in terms of the reversible complex permeability $\mu^*(f)$ in the 100 kHz to 1 GHz frequency range. The $\mu^*(f)$ spectra are analyzed into three elementary magnetization processes with changing weight factors as Cu content or sintering temperature T_{SINT} increase. In fact, in addition to the spin rotation relaxation at 150–400 MHz we initially identify the contribution from reversible domain wall bowing rising at 20–80 MHz. For higher Cu content or T_{SINT}, the latter mechanism is suppressed to the benefit of reversible wall displacement in the range below 1 MHz. Concerning particularly the domain wall motion, system dynamics theory and least-squares curve fitting of $\mu^*(f)$ spectra were employed to distinguish between the high-frequency underdamped resonance (d. wall bowing) and the lower frequency overdamped relaxation dispersions (d. wall displacement). This distinction originates in the microstructural variance between the pinned low-energy domain walls in individual small grains and the cooperative rigid high-energy walls in large grains, respectively. The relevant transition of morphology in NiCuZn ferrites, induced by Cu substitution or by high T_{SINT}, is identified through SEM observation and accords with the experimental results of dilatometry and density measurements. The remarked densification process is reflected on the increase of initial permeability as well. Moreover, on the basis of the recorded B–H loops we derive that the maximum induction B_{MAX} follows the density variation of sintered specimens, contrarily to the coercive field H_C which is significantly decreased when magnetic domain walls appear.

Keywords: D. Ferrites; Cu substitution; Complex permeability; Domain wall relaxation and resonance

1. Introduction

The introduction of Cu in the composition of cubic ferrites is a typical materials design technique in pursue of low-temperature densification [1,2]. This effect commences most probably due to the lattice diffusion of Cu ions [3,4] and is reinforced by the formation of a CuO phase at grain boundaries [5]. As a result, NiCuZn ferrites may be produced by low-temperature firing, whereas they additionally exhibit good electromagnetic properties in relatively high frequencies [6]. Furthermore, taking into account the economic aspect of ferrites manufacturing, we recognize the benefits gained by substituting Ni with Cu in the already massively produced NiZn ferrites. These special characteristics of NiCuZn spinels render them suitable for the fabrication of integrated planar electronic components (inductors, LC filters and transformers) compatible with microelectronics and surface mount technology (SMT) [7,8] and of EMI suppressing films operating in the 100 MHz to 1 GHz region [9,10].

With regard to the dynamic magnetic properties of ferrites, three basic reversible magnetization processes are discerned. Specifically, according to magnetic materials theory the magnetization under a low ac field is achieved through the rotation of magnetic moments within a domain along with the vibration and displacement of formed domain walls [11,12]. However, ambiguity rises about the origin and the type of domain wall motion as the latter mechanism is either not employed in the research of spinel ferrites or not further

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analyzed [13–15]. As the comprehension of frequency dependent magnetization processes in such magnetic ceramics is essential to design low-loss end products with tailored magnetic response, we have prepared and analyzed a set of NiCuZn ferrites in terms of their complex permeability in the 100 kHz to 1 GHz frequency range.

2. Materials and methods

The set of polycrystalline cubic ferrites that was selected for the present study is described by the nominal composition $Ni_{0.60-x}Cu_xZn_{0.40}Fe_{1.98}O_4$ with x=0, 0.10, 0.20 and 0.30 (samples N0, N1, N2 and N3 respectively). Since we intend to focus on the effects of Cu substitution for Ni, the Zn content was kept constant and equal to 0.40, which is expected to yield relatively high values of magnetization [11]. Additionally, Fe coefficient was adjusted to 1.98, which is reduced from the stoichiometric coefficient, as that promotes densification [3,5,16]. Despite the extent of the past research on NiCuZn ferrites, no relevant electromagnetic study on these specific compounds has been published.

The samples under test were prepared with the conventional solid-state reaction method starting from the proper oxides (NiO, CuO, ZnO and Fe_2O_3). The needed amounts of the precursors were initially ball mixed for 3 h in deionized water and dried at 100 °C for 24 h, followed by a heat treatment at 750 °C for 2 h with a heating rate of 5 °C/min. The prefired powder mixtures were further ball milled for 3 h and dried at 100 °C for 24 h and subsequently granulated with the addition of a plasticizer and lubricant compound (polyvinyl alcohol and Zn stearate, respectively). The granulated samples were then pressed under axial compaction (1350 psi) to form toroidal samples (outer/inner diameter: 23.5 mm/14.5 mm) with approximately 3 gr/cm^3 green density. Finally, in order to monitor the effect of sintering top temperature on certain properties of the end products, the ring-shaped samples were annealed for 3 h in air at temperatures varying from 1000 °C to 1200 °C.

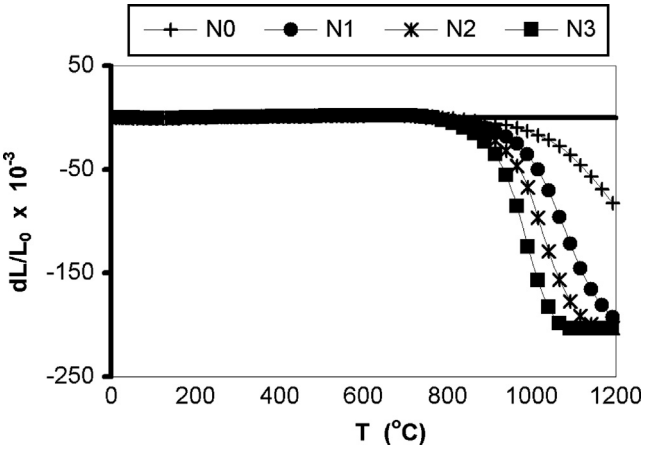

Fig. 1. Relative lengths change of prefired rods N0, N1, N2 and N3 with temperature.

For the phase and crystal structure identification of both prefired and sintered samples, the X-ray diffraction patterns were recorded (powder diffractometer Siemens D-500, CuKa). Moreover, the prefired powders were examined in terms of their particle size distribution (Malvern Mastersizer-S), whereas the shrinkage of pressed cylinders during annealing was measured by dilatometry performed up to 1200 °C (horizontal pushrod dilatometer Netzsch DIL 402PC). The microstructure of the sintered samples was studied by means of JEOL JSM6300 scanning electron microscope. Concerning the magnetic properties of these NiCuZn materials, we measured the B–H loops (10 kHz, maximum magnetic field 1200 A/m), the initial permeability (10 kHz, flux density 0.1 mT) and the complex permeability spectrum in the frequency range 100 kHz–1 GHz. All the magnetic measurements up to 1 MHz were conducted with an automated measurement apparatus which comprises Agilent 4284A Precision LCR meter, Tektronix TDS-714L Oscilloscope, Agilent 33120A frequency generator and the appropriate HF and RF amplifiers. For complex permeability measurements at frequencies from 1 MHz to 1 GHz, the Agilent E4991A RF Impedance Material Analyzer was used.

3. Results

3.1. Dilatometric, structural, and morphological characterization

Dilatometry is used to characterize the rod specimens of compacted prefired ferrite granules. By measuring the relative elongation/shrinkage along the longitudinal axis of rods during heating, useful information can be obtained regarding the densification and sintering process. Specifically, Fig. 1 depicts the measured length variation dL of the cylinders, normalized to their initial length L_0, with temperature up to 1200 °C. As a result, we initially derive that by increasing the Cu content either higher shrinkage is attained at the same heating temperature, or conversely, lower heating temperature is needed for the same shrinkage. In Table 1 we report the temperature where shrinkage first appears T_{INI} and the temperature of maximum shrinkage rate (maximum densification) T_{MAX}, which was extracted from the derivatives of the curves.

Table 1
Shrinkage parameters derived from dilatometry characterization. Here, T_{INI} and T_{MAX} are the temperatures where shrinkage begins and its rate is maximized, respectively.

	N0 (Cu: 0)	N1 (Cu: 0.10)	N2 (Cu: 0.20)	N3 (Cu: 0.30)
T_{INI} (°C)	661.9	661.8	662.0	661.9
T_{MAX} (°C)	1200	1058.8	1017.2	970.5