

High permeability Ni–Cu–Zn ferrites through additive-free low-temperature sintering of nanocrystalline powders

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Abstract

Nanocrystalline Ni–Cu–Zn ferrite powders $\text{Ni}_{0.20}\text{Cu}_{0.20}\text{Zn}_{0.62}\text{Fe}_{1.98}\text{O}_{3.99}$ were prepared by thermal decomposition of an oxalate precursor. The particle size is 6 nm and 350 nm, respectively, for powders obtained through calcinations at 350 °C or 750 °C. The shrinkage behavior significantly changes with particle size; the temperature of maximum shrinkage rate is $T_{\text{MSR}} = 700$ °C for particles of 6 nm size and increases to $T_{\text{MSR}} = 880$ °C for particles 350 nm in size. Dense samples with a permeability of $\mu = 780$ are obtained by sintering at 900 °C for 2 h. Mixtures of nanocrystalline and sub-micron powders allow tailoring of the shrinkage behavior. A maximum permeability of $\mu = 840$ is obtained after sintering of a 1:1-mixture at 900 °C. This demonstrates the potential of nanocrystalline ferrites for co-firing without additives at 900 °C and integration of ferrite inductors into LTCC modules.

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1. Introduction

Ni–Cu–Zn ferrites are used as standard soft magnetic materials for multilayer ferrite inductors (MLFI) because of their low sintering temperature and good performance up to MHz frequencies.^{1–3} The temperature for co-firing multilayer inductor components is restricted to 900 °C because silver is used as metallization. Correlations between the composition of Ni–Cu–Zn ferrites and their sintering behavior and magnetic properties have been investigated^{4–8} and optimum compositions for low-temperature ceramic co-firing (LTCC) of multilayer inductors can be selected. A typical feature of low-firing ferrite compositions seems to be a small deficiency of iron oxide, i.e. less than 50 mol% Fe_2O_3 is used in the starting mixture of oxides. Such compositions are referred to as sub-stoichiometric here; their composition typically translates into a spinel formula with less than two Fe per formula unit, e.g. $\text{Ni}_{0.20}\text{Cu}_{0.20}\text{Zn}_{0.62}\text{Fe}_{1.98}\text{O}_{3.99}$, compared to stoichiometric ferrites with 50 mol% Fe_2O_3 and two Fe per formula unit, e.g.

$\text{Ni}_{0.20}\text{Cu}_{0.20}\text{Zn}_{0.60}\text{Fe}_2\text{O}_4$. It was shown that Fe-deficient sub-stoichiometric compositions exhibit enhanced densification.⁹ Additionally, sintering additives are being used in order to enhance shrinkage and densification at 900 °C. Bismuth oxide has frequently been suggested as sintering aid for Ni–Cu–Zn ferrites.^{10–12} The addition of <1 wt% of Bi_2O_3 has been shown to be effective for preparing ferrites with a permeability as large as $\mu = 900$.^{13,14}

Another approach to obtain dense samples with optimized microstructures after firing at 900 °C is the use of sinter-active ferrite powders prepared by alternative synthesis routes. The precipitation of mixed oxalates and their subsequent thermal decomposition into ferrites is a classic alternative synthesis procedure of nanocrystalline ferrite particles.¹⁵ The oxalate route was already used to synthesize various nanocrystalline ferrite powders, e.g. magnetite,¹⁶ Mn–Zn ferrites,^{17,18} and Ni–Cu–Zn ferrites.¹⁹

In this contribution, we report on a systematic investigation of the synthesis and morphology of nanocrystalline Ni–Cu–Zn ferrite particles via the oxalate precursor route. We have studied the shrinkage, sintering behavior and microstructure formation upon firing at 900 °C. The permeability of the sintered samples was investigated as function of the powder particle

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size, and compared to that of ferrites made from standard sub-micron powders. The effect of dwell time during sintering at 900 °C on grain size and permeability is studied. Moreover, the potential of powder mixtures of nanocrystalline and sub-micron powders is evaluated. This method was already reported by Su et al. using nanocrystalline Ni–Cu–Zn ferrite synthesized via a sol–gel route.²⁰ However, no detailed information on individual powder particle sizes was reported. Moreover, the powder mixture was wet-milled until the average particle size was below 1 µm using stainless steel balls. The wear from the grinding media used in Ref. 20 is very likely to have increased the iron content upon milling and modified the ferrite composition and, hence, sintering behavior and permeability. It is demonstrated here, that the addition of nanocrystalline to sub-micron standard ferrite powders can be understood as application of an “internal” sintering aid. This is an approach to develop “external” (e.g. Bi₂O₃) additive-free Ni–Cu–Zn ferrites for integrated multilayer inductors. It has been shown, that the addition of Bi₂O₃ sintering aid to ferrites might have dramatic effects on the microstructure formation and hence permeability of Ni–Cu–Zn ferrite multilayer structures integrated into LTCC modules.²¹

2. Experimental

Ferrite powders of composition (NiO)_{0.20}(CuO)_{0.20}(ZnO)_{0.62}(Fe₂O₃)_{0.99}, i.e. Ni_{0.20}Cu_{0.20}Zn_{0.62}Fe_{1.98}O_{3.99}, were prepared by the oxalate precursor route. Fe-powder was dissolved in acetic acid under Ar-atmosphere to avoid the formation of Fe³⁺, a procedure already proposed by Wickham.¹⁵ Ni-, Cu-, and Zn-acetate-hydrates were dissolved in water and this mixed metal solution was added to the Fe-(II)-acetate solution. This mixed-cation solution is added to an oxalic acid solution in an argon atmosphere and a mixed-metal oxalate precipitate is formed. Co-precipitation and ageing for 2 h was performed at room temperature and at 70 °C. The oxalate powder is dried by removing the liquid in a rotary evaporator at 60 °C. The thermal decomposition of the mixed-metal oxalate was performed between 350 and 750 °C in Pt-containers without lids (powders referred to as oxalate350, . . . , 750).

A standard ferrite powder was prepared by the mixed-oxide route (powder oxide750). α-Fe₂O₃ (TKS Germany, HP grade) with a specific surface $S = 4.3 \text{ m}^2/\text{g}$; NiO (Inco, Black Nickel Oxide, Grade F) with $S = 70 \text{ m}^2/\text{g}$; CuO p. A. (Merck, Germany) with $S = 4.6 \text{ m}^2/\text{g}$ and ZnO (Harzsiegel Heubach, Germany, standard grade) with $S = 4.5 \text{ m}^2/\text{g}$ were used as starting materials. The oxides were wet mixed for 12 h in a polyethylene container. After drying the powder was calcined at 750 °C for 2 h and subsequently milled in a planetary ball mill using zirconia grinding media. Powder mixtures of nanocrystalline (oxalate350) and sub-micron (oxide750) powders were homogenized in a rotating PE container using water and zirconia grinding media (1 mm diameter) for 24 h. The ferrite powders were compacted using polyvinyl-alcohol as binder to give pellets for sintering studies or toroids for permeability measurements. The sintering was performed at 900 °C in air with a heating rate of 2 K/min up to

450 °C and 10 K/min to 900 °C and dwell times at 900 °C of 2, 4, or 12 h, respectively.

The phase formation of the materials was evaluated by XRD (Siemens D5000). The particle size of the powders was measured in an aqueous suspension using a laser diffraction system (Malvern Mastersizer 2000). The specific surface S of the powders was determined by nitrogen adsorption (BET, Nova 2000, Quantachrome Instruments, Boynton Beach, USA); a mean particle size (assuming spherical particles) was estimated using the relation $d_{\text{BET}} = 6/\rho \cdot S$ with the density ρ . The crystallite size was estimated from XRD line broadening using the Scherrer equation, $d_{\text{XRD}} = K\lambda/[(B - b) \cos \theta]$, with the wave length λ , the peak width B , the instrumental broadening b ($b = 0.08^\circ$ for standard LaB₆), the Bragg angle θ and the shape factor $K \approx 0.89$. Thermal analysis (TG, DTA) was carried out with a SETARAM TGA92 system, the samples were heated in open Pt containers (TG + DTA sample holder: diameter 3 mm, height 6 mm) in air with a rate of 2 K/min (sample mass about 20 mg). Shrinkage measurements were made with a Netzsch DIL402 dilatometer on cylindrical compacts during heating to 1000–1200 °C with 4 K/min heating rate. The bulk density of sintered samples was determined from the dimensions and weight. The powder morphology and the microstructure of the sintered samples were studied with a scanning electron microscope (SEM, Zeiss DSM940A). The permeability of the sintered toroids was measured using an impedance analyzer in the frequency range 1–1000 kHz. For frequencies up to 2 GHz permeability measurements were performed using an Agilent E4991A impedance/materials analyzer.

3. Results and discussion

3.1. Synthesis of nanocrystalline Ni–Cu–Zn ferrite powders

The co-precipitated Ni–Cu–Zn–Fe oxalate hydrates are yellowish powders with an orthorhombic β-oxalate structure as shown by X-ray diffraction (not shown here). Thermal decomposition of the mixed oxalate hydrate in air is almost complete at 300 °C (Fig. 1). The DTA curve exhibits an endothermic peak at 150 °C as signature of the dehydration step and an exothermic peak at 270 °C corresponding to the oxalate decomposition reaction. The temperature of Ni–Cu–Zn–Fe oxalate precipitation has a dramatic influence on the particle morphology. Whereas mixed oxalates precipitated at room temperature exhibit a homogeneous particle size of about 0.5 µm with little formation of hard aggregates (Fig. 2a), the mixed-metal oxalates precipitated and aged at 70 °C form 2 µm large star-like aggregates (Fig. 2b). The oxalate aggregate morphology is kept during the thermal decomposition process. The morphology of the decomposition products is similar to those of the oxalates (Fig. 2c and d). This topotactic transformation behavior is typical of precursor decompositions and was already reported for other oxalate to ferrite transformations.^{16,18} Since a fine-grained oxide powder is obtained only through thermal decomposition of oxalate particles precipitated at room temperature, the following studies were performed with these mixed-metal oxalates.

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