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Frequency behaviour of Zn–Mn ferrites nanoparticles obtained by high-energy ball milling

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Abstract

Zinc–manganese spinel ferrites have been obtained by high-energy ball milling from precursors (1) oxides and carbonates and (2) acid oxides and hydroxides. Results reveal that the use of one or another precursor leads to final products with different structural and magnetic characteristics. Measurements of the domain wall relaxation frequency exhibited differences depending on the type of precursor. These results are interpreted in terms of the variations in the magnetocrystalline anisotropy between the samples. © 1999 Elsevier Science B.V. All rights reserved.

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The frequency dependence of magnetic permeability, μ, in ferrites is of technological importance especially taking into account those where the use of high-frequency AC fields is required [1]. It is well known that, for a given composition, the domain wall relaxation frequency, f_x (and therefore, the frequency range below which μ retains a high value) is inversely dependent [2] on grain size of the sample. On the other hand, for different compositions, f_x is proportional to the magnetocrystalline anisotropy [3].

The initial magnetic permeability is a microstructure-sensitive property. The study of the thermal variations of initial permeability of polycrystalline ferrites can be used as a quality test in the preparation of ferrite samples [4]. At the Curie point the initial permeability drops from a value (generally its maximum) to near 1. The slope of this drop provides an evaluation of the sample's chemical homogeneity [5].

In this paper, we have used initial permeability measurements as a function of temperature and frequency, to investigate the chemical homogeneity and relaxation range of nanocrystalline ferrites synthesised by mechanical alloying from two different precursors.

The final product with nominal composition $Zn_{0.40}Mn_{0.56}Fe_{2.04}O_4$ was prepared by high-energy ball milling using two different precursors: (1) oxides and carbonates and (2) hydroxides and oxides. After winding a low-capacitance coil [6], their impedance response was measured in the 5 Hz–13 MHz frequency range by means of a system including a HP4192A impedance analyser. Complex permeability was derived from impedance measurements by means of

$$\mu^* = KL^* = K(-\mathrm{j}/\omega)Z^* \quad (1)$$

where K is the geometrical constant for toroids, L the complex inductance ($L^* = L_r + L_i$), $\mathrm{j} = (-1)^{1/2}$, ω the angular frequency ($\omega = 2\pi f$), and Z^* the complex impedance.

XRD patterns (Fig. 1) show a single spinel phase with broad diffraction peaks. The broad shape of the maxima reflected the formation of a disordered structure, with small crystallite size (8–17 nm) and strong internal strains introduced by the mechanical treatment. After annealing, an increase in crystallite size is observed as a consequence

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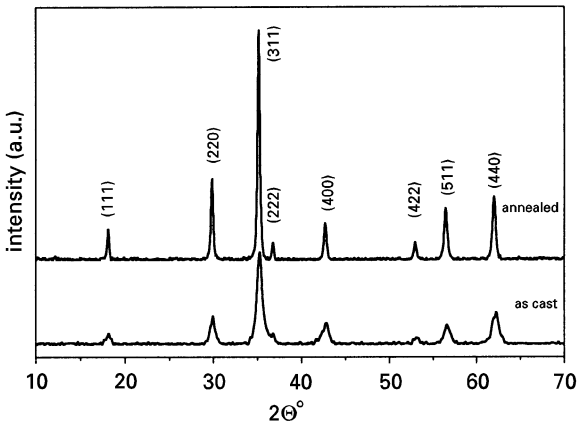

Fig. 1. XRD patterns for samples 1 and 1′. Indices for spinel structure are indicated.

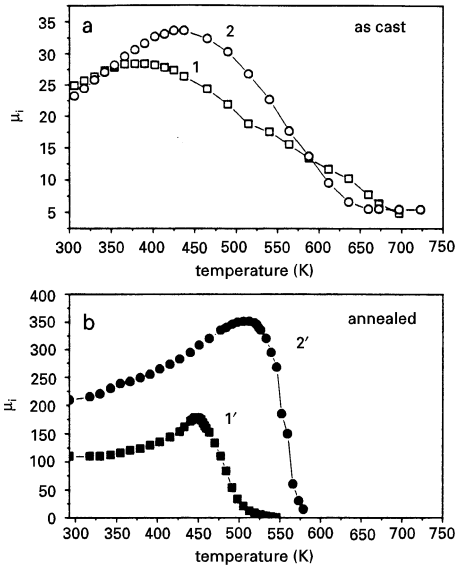

Fig. 2. The initial magnetic permeability of samples (a) 1 and 2, (b) 1′ and 2′.

of the relaxation of the structure. Relaxation energies between 20 and 40 kJ mol^{-1} have been reported [7].

Chemical homogeneity was qualitatively determined by the drop of μ as a function of temperature (Fig. 2). Ferrites 1 and 2 showed a very low μ, in agreement with the small grain size observed by SEM (about 0.2 μm). After reaching a maximum at 400 and 430 K for samples 1 and 2, respectively, μ drops in a wide range of temperature ($\sim$150 and $\sim$ 112 K for types 1 and 2, respectively) showing a high degree of chemical inhomogeneity and

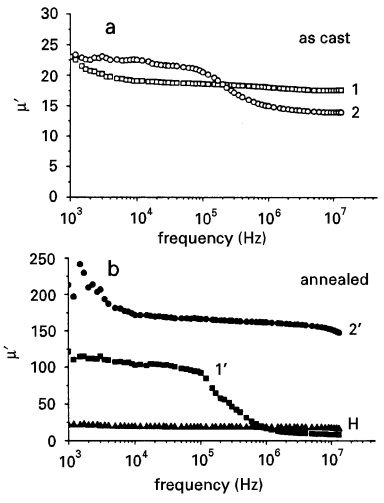

Fig. 3. Real part of permeability as a function of frequency for (a) samples 1 and 2, (b) samples 1′, 2′ and measures taken under a DC magnetic field (H).

well below the T_c values (550 K) as expected for this composition [8].

Fig. 2 also shows the effects of annealing on initial permeability. It is clear from these curves that a homogenisation process take place. The Curie point is increased in both samples (498 and 543 K for samples 1′ and 2′, respectively) as well as the verticality of the drop at this point (within $\pm$ 29 and $\pm$ 35 K, respectively). The annealing resulted in ferrites with higher μ values, more homogeneous and with T_c values close to the expected ones. These curves showed that the milling process is assisted by using precursors of type 2, therefore the dissolution of Mn^{2+} into the spinel structure is higher compared with the ferrites obtained from precursors of type 1. This is clear from the higher chemical homogeneity shown by the drop at the Curie point for type 2 samples (both as-cast and annealed), as well as by the higher Curie temperature, which points out a higher Mn : Zn ratio into the magnetic phase.

Fig. 3 shows the behaviour of μ as a function of frequency for samples 1 and 2. The low-permeability values are a consequence of the small grain size and the structural disorder induced by milling. Measurements performed under a DC field showed the same values of μ, which points out to the formation of monodomain particles. No significant dissipation process was observed over the whole frequency range. We assume that the small variations observed as frequency increases are a consequence of the chemical inhomogeneity of these ferrites.

Annealed samples showed higher μ values as well as a multidomain structure arrangement. This is clear from

the dissipation phenomena observed at $\approx 10^5$ Hz for sample 1′ and the drastic decrease of μ when measurements are carried out under a DC magnetic field. The dissipation effects in sample 2′ could be expected at frequencies above the upper limit (13 MHz) of our measuring system.

In agreement with the behaviour of μ as a function of temperature, these data point out to a higher degree of homogenisation of sample 2. The dissolution of Mn into the spinel structure led to an enhancement of the magnetocrystalline anisotropy as well as in the T_c value. This led to an increase of the domain wall relaxation frequency. The presence of a hydroxide and an acid oxide (samples 2 and 2′) therefore seems to assist the incorporation of cations during the milling process as well as during the subsequent annealing. It could be explained by an acid/base reaction that would take place during the mechanical alloying.

Nanocrystalline Zn–Mn spinel ferrites have been obtained by high-energy ball milling from two different precursors.

The correlation between Zn–Mn ratio with Curie point as well as the drop of permeability at this point (closely related with the chemical homogeneity) indicated a non homogeneous incorporation of Mn^{2+} in the spinel structure. Thermal treatments led to a more homogeneous ferrites.

The differences in the relaxation frequency range can be explained by the corresponding differences in magneto-crystalline anisotropy among these ferrites, due to the different dissolution degree of Mn^{2+} into the spinel structure. The incorporation of Mn^{2+} is assisted by the presence of a hydroxide and an acid oxide as precursors.

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