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Electrical and magnetic behaviour of nanostructured $MgFe_2O_4$ spinel ferrite

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ABSTRACT

Nanostructured $MgFe_2O_4$ spinel has been synthesized with various grain sizes ranging from 72 to 19 nm using ceramic method and followed by high-energy ball milling. The observed electrical conductivity decreases with grain size is mainly due to the size effect than the cation distribution which is clearly evident by in-field Mössbauer measurement. The saturation magnetization of the 72 nm grain size sample has been enhanced and it is about 39% larger than that of their bulk (micron size particle). The observed increase in the coercivity of the milled sample is due to the smaller crystalline size, increase in the grain boundary volume and also due to surface anisotropy of increasing number of ions on the surface.

1. Introduction

Nanoparticles of spinel ferrites are potential candidates in the field of magnetic and electronic applications. They have wide applications in drug delivery systems and in medical diagnostics [1]. Spinel ferrites have high electrical resistivities and low dielectric losses which are useful in microwave devices, computer memories and magnetic recording. Among the spinel ferrites family, magnesium ferrite is a soft magnetic n-type semiconducting material [2], which finds a number of applications in sensor technology, thermal coagulation therapy, in which tumors are locally heated by application of alternating magnetic fields [3]. The structural formula of $MgFe_2O_4$ is generally written as $(Mg_{1-\lambda}Fe_\lambda)[Mg_\lambda Fe_{2-\lambda}]O_4$, where parentheses and square brackets indicate cation site of tetrahedral (A) and octahedral [B] coordination, respectively, and where λ represents the degree of inversion defined as a fraction of (A) sites occupied by Fe^{3+} ions.

In recent years, nanosized milled spinel ferrites exhibit interesting magnetic and electrical properties which are different from those of the bulk counterparts. The variation of the Néel temperature with grain size [4,5], a high coercivity [6] and enhanced magnetic moments [7,8] has been observed in nanosized ferrite particles compared with those of bulk samples. The Néel temperature of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ spinel ferrite was shown to increase from 538 K in the bulk state to 611 K when the grain size was reduced to 14 nm using high-energy ball milling [9]. In the past five decades, impedance spectroscopy is used to investigate the dynamics of bound and/or free ions in the bulk or in the interfacial regions of any kind of solid or liquid materials such as ionic, semiconducting, mixed electronic–ionic and dielectrics. The dispersion in conductivity has been seen in a broad variety of disordered solids like, amorphous semiconductors, ionic and electronic conducting polymers, ion conducting glasses, highly defective crystals or doped semiconductors and single crystals [10–14]. Ponpandian et al. [15] have reported that the real part of dielectric constant (ε') and dielectric loss ($\tan\delta$) for milled samples are about two orders of magnitude smaller than those of bulk in the case of $NiFe_2O_4$.

Several reports are available in the literature on the magnetic properties of nanoscale $MgFe_2O_4$ [16–22]. A few investigators have studied the electrical properties in the case of bulk $MgFe_2O_4$

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[23–25]. This has motivated us to carry out electrical conductivity and dielectric measurements on nanostructured $MgFe_2O_4$. In order to explain the results obtained from the electrical conductivity and dielectric measurements, we have also performed in-field Mössbauer spectroscopy and magnetization measurements. We have, therefore, studied the effect of grain size, temperature and frequency on the electrical and magnetic properties of $MgFe_2O_4$ spinel prepared using the ceramic route and followed by high-energy ball milling.

2. Experiment

2.1. Sample preparation

The bulk $MgFe_2O_4$ spinel ferrite has been synthesized using the ceramic method. Stoichiometry mixtures of powdered reactants containing α-Fe_2O_3 and MgO were thoroughly mixed in the atomic ratio 1:1. The mixed sample was calcined at 1173 K in air and kept at this temperature for 5 h, which was furnace cooled to room temperature (300 K). The cold ferrite powder was then thoroughly ground in an agate mortar and pelletized. The pellet was then sintered at 1573 K for 5 h. The pellets were reduced to powders using agate mortar and taken to be the as-prepared sample. The as-prepared sample was milled for 10 and 15 h using planetary high-energy ball mill (Fritsch pulverisette 7) with zirconia vials and balls. The milling speed of vials and balls was 300 rpm with a ball to powder weight ratio of 8:1.

2.2. Sample characterization

The phase analysis for the as-prepared and milled samples was carried out using X-ray diffraction (XRD) with a Rigaku-make high precision Guinier X-ray diffractometer and Fe Kα radiation. The average grain size was determined from the full-width at half-maximum of the (3 1 1) reflection of the XRD patterns using Scherrer's formula [26]. Surface morphological features of the as-prepared and milled samples were observed using a field emission scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan).

2.3. Electrical and magnetic measurements

The electrical conductivity and dielectric measurements were done using an impedance analyzer (Solatron 1260 Impedance/Gain-Phase Analyzer) in the temperature range from 300 to 550 K and in the frequency range from 1 Hz to 10 MHz. The powder was made into a pellet by applying a pressure of 50 MPa for these measurements and the sample was sandwiched between two platinum electrodes. In order to homogenize the charge carriers and to remove the moisture content, the pellet was preheated up to 423 K for 30 min, before starting the measurements. The real (Z') and imaginary (Z'') parts of the complex impedance (Z^*) were measured as a function of both frequency and temperature. The temperature of the sample was measured with a resolution of ±1 K using a Eurotherm (818 P) PID temperature controller, the heating rate being 2 K/min. The conductivity (σ), the real (ε') part of dielectric constant and dielectric loss, $\tan\delta$ were calculated using the raw data of Z' and Z'' and the sample dimensions.

Magnetic measurements were made using a vibrating sample magnetometer (Model: EG&G PARC 4500, USA) (VSM). The ^{57}Fe Mössbauer spectra were recorded at 10 K under a magnetic field of 8 T applied parallel to the γ-ray direction. The degree of inversion was calculated from the subspectral areas ($I_{(A)}/I_{[B]} = f_{(A)}/f_{[B]} \times x/(2-x)$), assuming that the ratio of the recoilless fractions is $f_{(A)}/f_{[B]} = 1$ at low temperatures [27].

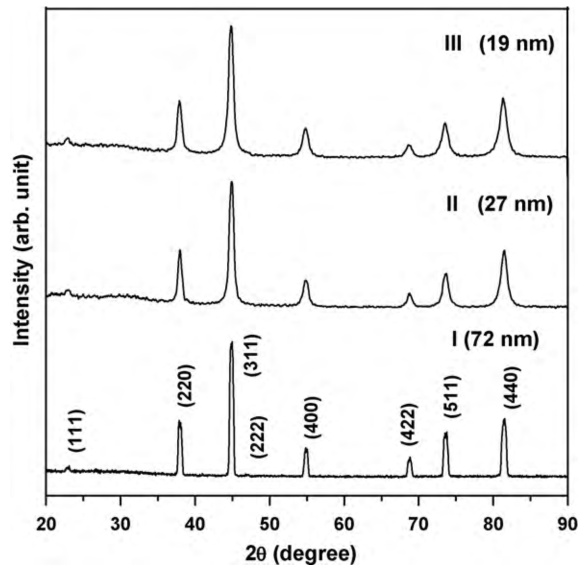

Fig. 1. The XRD patterns of $MgFe_2O_4$ spinel samples: (I) as-prepared, (II) 10 h milled, and (III) 15 h milled.

3. Results and discussion

3.1. Structural analysis and surface morphology

Fig. 1 shows the X-ray diffraction patterns of the as-prepared (sample I), the 10 h milled (sample II) and the 15 h milled (sample III). The increase in the broadening of the X-ray diffraction lines gives a clear evidence for the decrease of the mean size of the milled sample. The average grain size has been calculated using Scherrer's formula by taking into account the instrumental line broadening. The average grain sizes were found to be 72, 27 and 19 nm for samples I, II and III, respectively. The microstructure of $MgFe_2O_4$ for as-prepared, 10 and 15 h milled samples are shown in Fig. 2(I), (II) and (III), respectively. The particle size of as-prepared (I) is found to lie in the range 12–23 μm. In the case of 10 h (II) and 15 h milled (III) samples, the particles are around 280–340 nm and 220–260 nm, respectively.

3.2. Electrical behaviour

3.2.1. Dc conductivity and its dependence on grain size

Fig. 3 shows the Arrhenius plot for the electrical conductivity of samples I–III in the temperature range from 370 to 500 K. The resistance was obtained by analyzing the impedance data using the non-linear least-squares (NLLS) fitting routine. The variation in conductivity with the inverse temperature is almost linear in all cases. The conductivity is found to increase with temperature for all samples, which is expected from the semiconducting behaviour of spinel ferrites, as observed earlier [9,15]. $MgFe_2O_4$ is reported to be an n-type semiconductor [2], due to the hopping of electrons from Fe^{2+} to Fe^{3+} ions in the octahedral [B] sites. The activation energy for the electrical conductivity is obtained from the Arrhenius relation,

$$\sigma T = \sigma_0 \exp\left[-\frac{E_a}{k_B T}\right] \quad (1)$$

where σ_0 is the pre-exponential factor with the dimensions of ($\Omega\,cm^{-1}$)K, E_a is the activation energy for dc conductivity and k_B is the Boltzmann constant. Table 1 shows the values of activation energies obtained for samples I–III. We have observed that the activation energy increases with the grain size reduction, which reflects the blocking nature of grain boundary [10]. The blocking nature of the grain–grain contacts was suggested to be due to the seg-