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Effect of preparation on magnetic properties of Mn-Zn ferrite[†]

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Mixed ferrites belonging to the type $Mn_{0.9}Zn_{0.1}Fe_2O_4$ have been prepared by the double sintering method and by the chemical co-precipitation for comparing their magnetic properties. Sintered and precipitated ferrites exhibit different characteristics, especially in their magnetic properties like magnetization (M_s), coercive field (H_c) and Curie temperature (T_c). The sintered particles were size reduced in order to compare with the nanosized co-precipitated particles. The effect of grinding has also been studied. Particles have been collected at regular intervals of grinding and their properties have been studied. The increase in the coercive field has been recorded by a hysteresis curve tracer confirming size reduction. X-ray diffraction studies confirmed the structure and consequent size reduction.

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Of all the ferrites, Mn-Zn ferrites are the most commercially important class of material. One can aim at lowering the Curie temperature of $MnFe_2O_4$ by replacing the Mn ion from the A site with a non-magnetic ion such as Zn. The substitution of Zn ion may increase the saturation magnetization and reduce the Curie temperature if the cation distribution is not altered[1]. In this paper, we report the change in Curie temperature along with other magnetic properties of $Mn_{0.9}Zn_{0.1}Fe_2O_4$ fine particles due to the effect of grinding and the preparation by two different techniques. The interest to study the effect of grinding is to prepare ferrofluids by ball milling, suitable for such of those fluids, which cannot be prepared by chemical method. Preparation procedure for substituted ferrites, as ferrofluids is not that much easy and there is a critical limit for the percentage substitution. The properties like particle size, saturation magnetization and Curie temperature by chemical method depend on the preparation conditions[2]. Ferrofluid preparation by ball milling is the other option to synthesise fluids having various substituted ferrites.

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Experimental Procedure

Preparation

Generally a number of techniques were used to prepare fine particles, but here we used the double sintering method and standard co-precipitation technique. Fine particles of $Mn_{0.9}Zn_{0.1}Fe_2O_4$ were prepared after ball milling the sintered powders. Sintering of the precursors (purity 98.5%) in their correct stoichiometric ratio was carried out using double sintering technique. The precursors were initially mixed thoroughly and pre-fired twice at about 600°C. The samples were finally heated up to 1000°C for nearly 12 h and allowed to cool in the oven itself. Finally sintered products were size reduced by PM400 Planetary type ball mill using agate jars and balls. The ball is to weight ratio was maintained as 10:1 for effective grinding[3]. Wet method was adopted and acetone was used as the grinding medium. The samples were collected at periodic intervals for analysis and characterization.

Fine particles were obtained directly by chemical co-precipitation technique by adding the respective molar salt solutions to 8 M NaOH solution at an elevated temperature around 80°C with constant stirring. The precipitate was washed with distilled water many times and finally washed with acetone and dried in air.

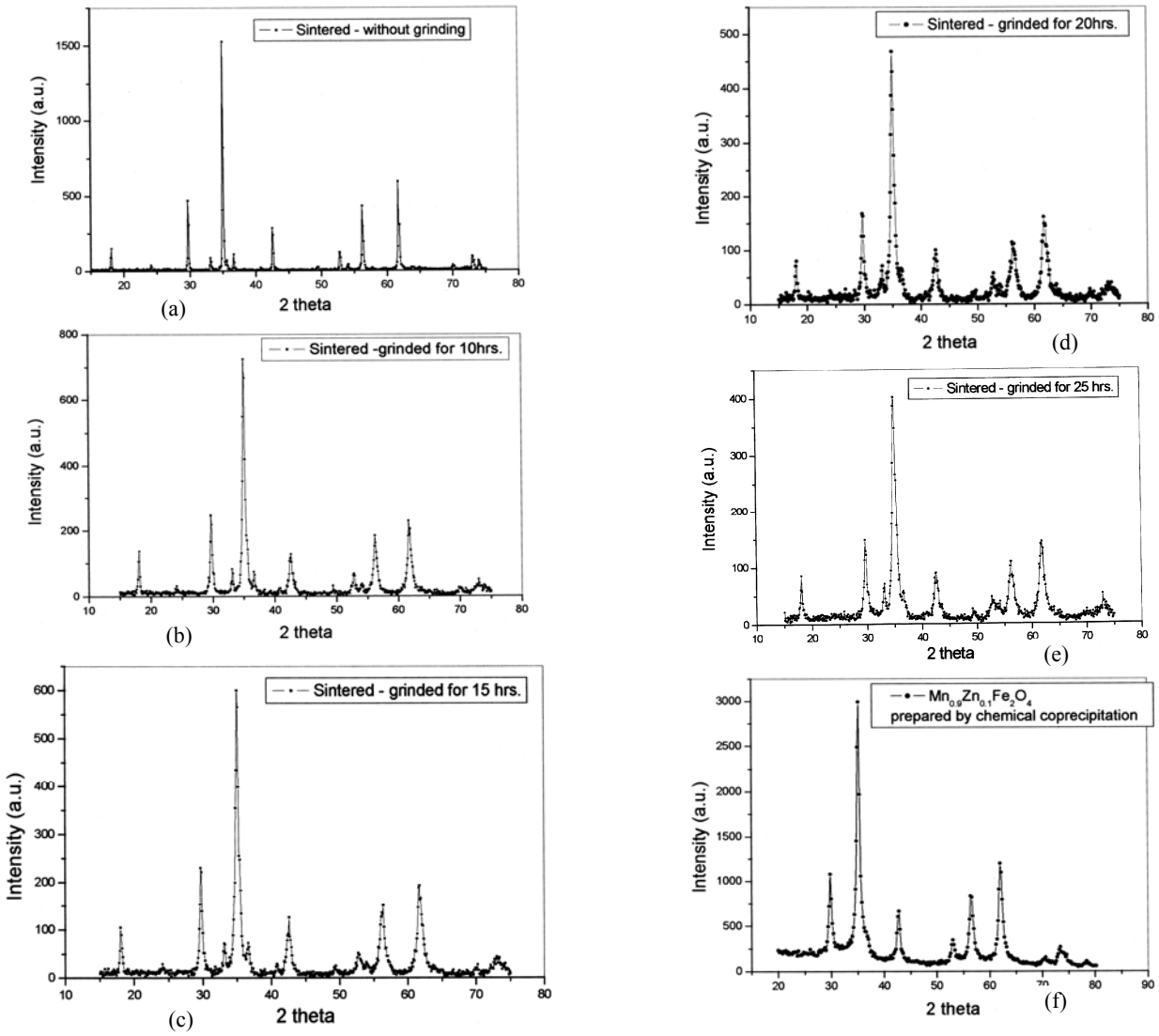

Fig. 1—Sintered $Mn_{0.9}Zn_{0.1}Fe_2O_4$ (a) without grinding, (b) grinded for 10 h, (c) grinded for 15 h, (d) grinded for 20 h, (e) grinded for 25 h and (f) $Mn_{0..9}Zn_{0.1}Fe_2O_4$ particles prepared by chemical coprecipitation method.

Structural characterization

X-ray diffractometer having CuKα radiation (λ=1.5418 Å) was used in structural characterization. The particle size was calculated using Scherrer's formula by using the full width at half maximum (FWHM) intensity of (311) plane of the pattern. The broadening of the peak confirms size reduction and the recorded spectrum for different hours of grinding (Figs 1a-e). The two theta value of the (311) plane, full width half maximum value of the (311) plane calculated using a scientific peak fit software and calculated particle size using the measured FWHM values are given in Table 1. The satellite reflections found in the XRD pattern are due to the impurities from the precursor, as they are only 98.5% pure and are not by the contamination during the grinding process.

Magnetization measurements

The magnetization, remanence and coercivity measurements at room temperature were carried out by pulse field technique. This pulse field set-up has a limitation of maximum field of 1000 Oe. The change in magnetization of the prepared samples by both the techniques were obtained till the sample's, Curie temperature. Table 2 gives the values of coercive field, remanence and Curie temperature. To avoid rotation the particles are encapsulated tightly and placed in a magnetic field. To check whether rotation occurred, the capsule was placed in different position and coercivity was measured. Fig. 2 shows the nature of the change in magnetization of the sample with respect to temperature till its Curie temperature is reached.

Results and Discussion

In recent years, high-energy ball milling techniques have demonstrated the ability to produce a variety of alloys and compounds, which may be crystalline or amorphous[3]. We have used this high-energy ball milling technique to produce nanosized ferrite particles and ferrofluids out of it. It has been reported that continuous grinding of nearly 500 h is required for the preparation of ferrofluids by ball milling[4]. But by the use of high-energy ball mill we have prepared ferrofluids within 30-40 h of grinding. At present, we have studied the changes in the magnetic properties at room temperature during the process of grinding and compared them with the sample prepared by the chemical method.

Particle size determination

Recorded XRD patterns are given in Figs 1a-e. The patterns show that the particles have a spinal structure. The broadening of the peak suggests the formation of small crystallites. The particle size is calculated using Scherrer's formula by using the full width at half maximum intensity of (311) plane. Fig. 3a shows the reduction in particle size with respect to the grinding time. From this figure, it is clear that the size reduction is not varying linearly with the grinding time. As the milling time increases, the average grain size initially drops from about 47 nm to 14 nm in 10 h. and thereafter it does not show much variation even after 20 h of grinding. As milling progresses the grain size is initially expected to be reduced. Afterwards, since reduction to the atomic level cannot proceed, the sample is size reduced to a limiting value.

Table 1—Particle size calculated for the samples prepared by two different techniques and for different hours of grinding

Preparation / Period of grinding	2θ value of (311) plane	FWHM value of (311) plane	Particle size (nm) calculated by Scherrer's formula
Sintered – without grinding	35.019	0.176	47
Sintered – 10 h of grinding	35.030	0.546	14
Sintered – 15 h of grinding	35.041	0.716	12
Sintered – 20 h of grinding	35.050	0.868	10
Sintered – 25 h of grinding	35.063	0.965	9
Chemical method	35.30	0.617	13

Table 2—The difference in magnetic properties of the samples prepared

Preparation / Period of grinding	Hc Oe	Mr emu/g	Magnetization at 1000 Oe emu/g	Particle size (nm) calculated by Scherrer's formula
Sintered – without grinding	10.61	0.77	50.68	47
Sintered – 10 h of grinding	16.67	0.95	62.53	14
Sintered – 20 h of grinding	62.12	4.78	60.78	10
Sintered – 25 h of grinding	72.73	5.46	49.14	09
Chemical method	71.21	5.2	51.50	13

Magnetization measurements

Even though much variation in the particle size is not achieved by long duration of grinding, it does affect the magnetic properties of the samples. The samples after ball milling exhibit much larger values of *H*c. Hysteresis loop of sintered $Mn_{0.9}Zn_{0.1}Fe_2O_4$ and that prepared by chemical method are shown in Figs 4a-e. A comparison of Figs 4a-d shows that the increase in coercivity and remanence is a direct result of the decrease in particle size. But the magnetization at 1000 Oe decreases as the size of the particle decreases. This can be attributed to the spin canted surface layer due to the fine size of the particles. The magnetization has increased after 10 h of initial grinding. The average particle size after 10 h of grinding is about 14 nm and the increase in magnetization may be due to the completion of diffusion of cations in their respective sites. The observed reduction in the magnetization value on further grinding is due to the size effect.

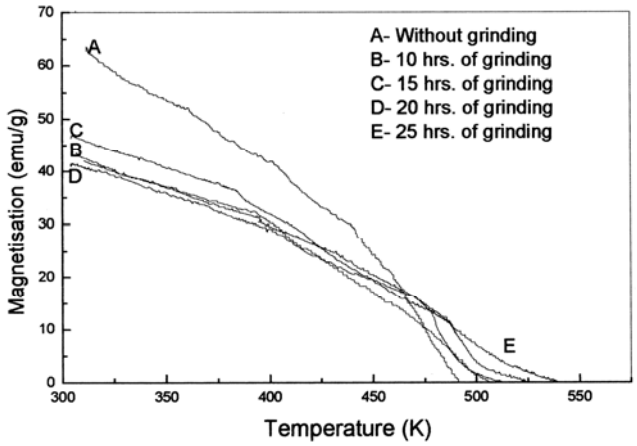

Fig. 2 —Curie temperature of the (sintered) grinded samples

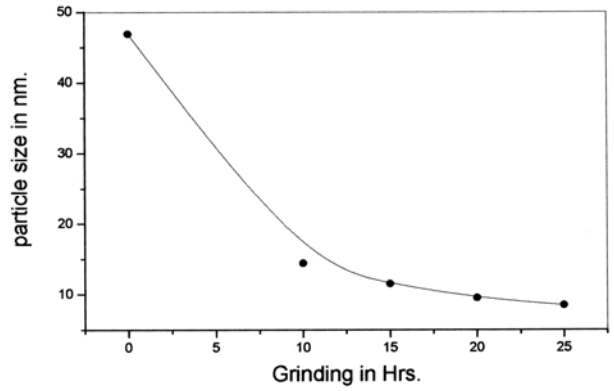

Fig. 3a—Reduction of particle size with grinding time in hours.

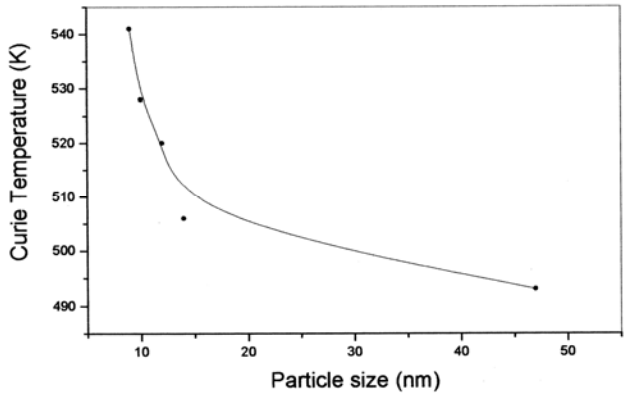

Fig. 3b—Change in Curie temperature with particle size

In the ceramic method, sintering of ferrites is carried out at high temperature (~1000-1100°C). At this temperature range, the rate of diffusion of cation is sufficiently high and a perfect crystalline lattice with high chemical homogeneity is formed. Ultra fine $Mn_{0.9}Zn_{0.1}Fe_2O_4$ particles have been prepared by chemical method at temperature near 100°C and their properties have been found to differ from the corresponding sintered ferrites. $Mn_{0.9}Zn_{0.1}Fe_2O_4$ particles of 12-20 nm contain up to 10wt.% of associated water, which cannot be eliminated by heating in aqueous solution at 100°C[5]. Though the particle size of the sample prepared by the chemical method is closer to the sintered sample after the initial 10 h. of grinding, the value of the magnetization is not comparable with chemical method. The decrease in the observed value for the chemically prepared sample is attributed to the associated water of hydration along with the effect of spin canted surface layer.

Curie temperature measurements

The Curie temperature of the samples investigated with its particle size is given in Table 3. We have

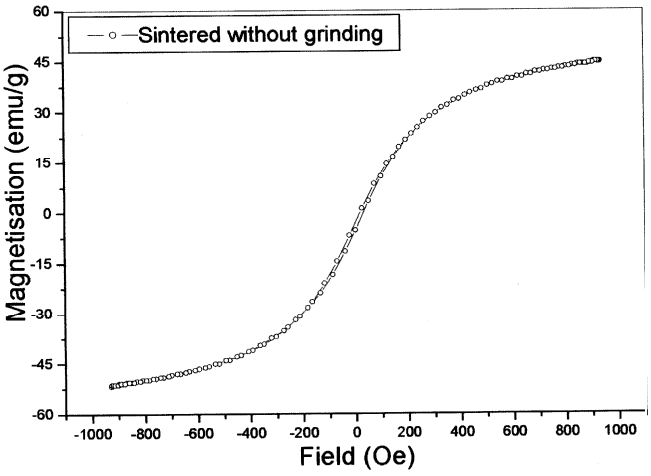

Fig. 4a—Magnetic hysteresis loop of sintered $Mn_{0.9}Zn_{0.1}Fe_2O_4$ (47 nm) Maximum field applied 1000 Oe

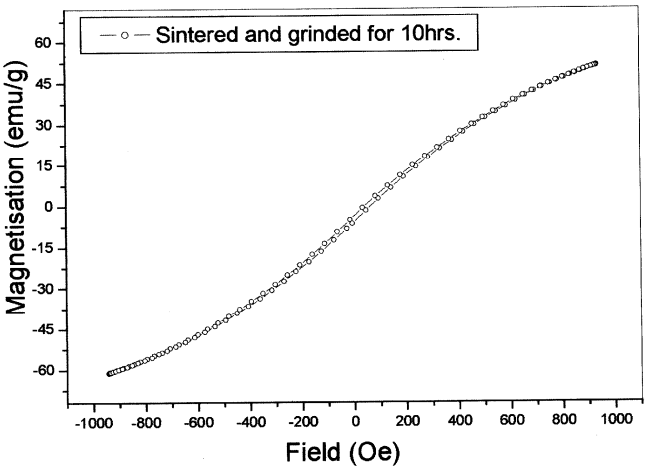

Fig. 4b—Magnetic hysteresis loop of sintered $Mn_{0.9}Zn_{0.1}Fe_2O_4$ (14 nm) Maximum field applied 1000 Oe

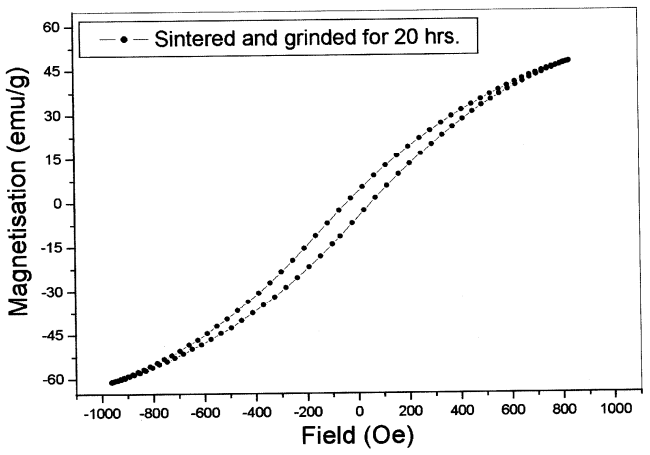

Fig. 4c—Magnetic hysteresis loop of sintered $Mn_{0.9}Zn_{0.1}Fe_2O_4$ (10 nm) Maximum field applied 1000 Oe

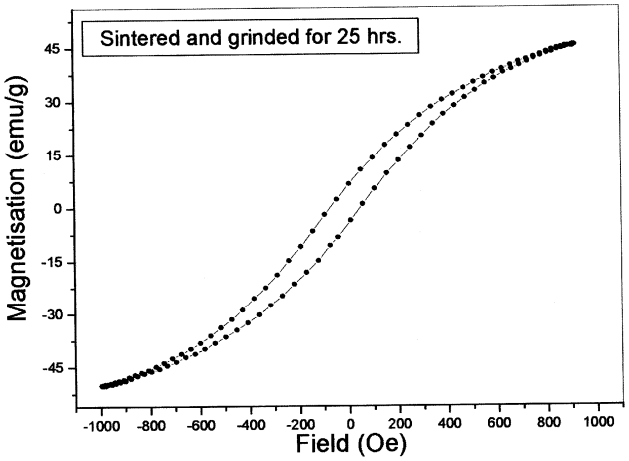

Fig. 4d—Magnetic hysteresis loop ofsintered $Mn_{0.9}Zn_{0.1}Fe_2O_4$ (9 nm) Maximum field applied 1000 Oe

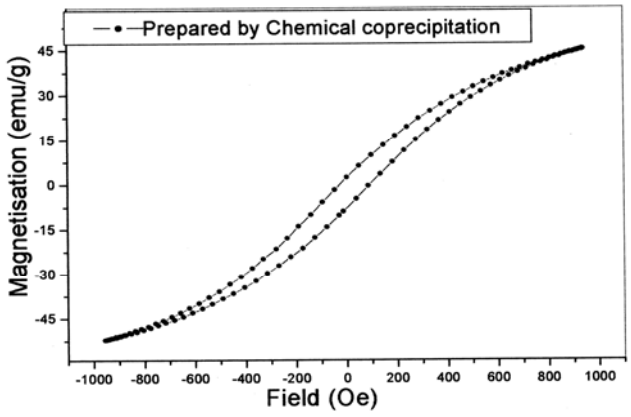

Fig. 4e—Magnetic hysteresis loop of chemically prepared $Mn_{0.9}Zn_{0.1}Fe_2O_4$ (13 nm) Maximum field applied 1000 Oe

observed that there is an enhancement in *T*c with decreasing particle size. The variation in the Curie temperature observed in the sintered samples for various particle sizes is plotted in Fig. 3b. The chemically prepared sample showed an increase in its Curie temperature when examined after being heated for the estimation of water content. The associated water content of the chemically prepared samples were estimated by heating the sample to a higher temperature and the change in weight being measured by a micro balance. In order to explain this increase in *T*c, one has to analyse the kinetics of cation redistribution taking place during the heating process to remove the associated water content. The non-equilibrium distribution of cations by the wet chemical method and cation redistribution taking place after heating of the sample causes the increase in the value of *T*c.

Table 3—The change in Curie temperature with the effect of preparation

Preparation/Period of grinding	*T*c, K	Particle size, nm
Sintered – without grinding	493	47
Sintered – 10 h of grinding	506	14
Sintered – 15 h of grinding	520	12
Sintered – 20 h of grinding	528	10
Sintered – 25 h of grinding	541	09
Chemical method	498	13
Chemical method Associated water content 9.2 wt%	574	-
Chemical method Associated water content 2.7 wt%	585	-
Chemical method Associated water content 2.4 wt%	607	-

Conclusions

The magnetic properties of the $Mn_{0.9}Zn_{0.1}Fe_2O_4$ nanoferrites depend mainly on its preparation conditions. Hence to prepare ferrofluids by ball milling one has to study the effect of grinding on the magnetic properties of the dispersed particles. The effect of grinding does not affect the Curie temperature much when compared with the chemically prepared samples. The Curie temperature is increased by 48°C when the size of the sample is reduced by nearly 30 nm. But there is an increase of about 109°C after being heated to a temperature of about 400°C to reduce the associated water content from 9% to 2%.

The work is being continued to determine cation distribution to ascertain whether increase in *T*c is due to cation redistribution and to study further the effect of grinding and annealing on the magnetic properties of chemically prepared MnZn ferrites.

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