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$Mn_xZn_{1-x}Fe_{2-y}R_yO_4$ (R = Gd, Eu) Ferrite Nanocrystals for Potential Magnetocaloric Applications

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ABSTRACT

The use of a ferromagnetic fluid for cooling applications represents an encouraging alternative to traditional methods; the fact that the fluid can be pumped with no moving mechanical parts, using the magnetocaloric effect, can be a great advantage for many applications where high maintenance costs and power consumption are undesirable. The nanocrystalline material suitable for this specific application must exhibit certain specific properties, such as tunable Curie temperature (T_c) and high saturation magnetization (M_s). The present work is focused on the aqueous synthesis and characterization of Mn-Zn ferrite nanocrystals and their subsequent doping with rare-earth elements (Gd and Eu ions), as an attempt to modify the T_c. SQUID characterization of ferrite nanocrystals showed that room temperature M_s and the corresponding T_c values were strongly dependent on the type and amount of the dopant species.

Keywords: Ferrites, magnetocaloric applications, doping, Curie temperature.

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1. INTRODUCTION

A magnetocaloric pump provides a simple means of pumping fluid using only external thermal and magnetic fields. The principle, which can be traced back to the early work of Rosensweig [1], is straightforward. Magnetic materials tend to lose their magnetization as the temperature approaches the material's Curie point. Exposing a column of magnetic fluid to a uniform magnetic field coincident with a temperature gradient produces a pressure gradient in the magnetic fluid. As the fluid heats up, it loses its attraction to the magnetic field and is displaced by cooler fluid. The impact of such a phenomenon is obvious: fluid propulsion with no moving mechanical parts [2]-[3]. The ideal nanocrystal for this application should have a Curie temperature near the maximum operating temperature of the system coupled with high magnetization and pyromagnetic coefficient values to maximize the pressure gradient in the fluid. Most commercially available ferrofluids are based on magnetite particles with a Curie temperature of 860K, which makes this ferrofluid undesirable for some applications in which the operational temperature is far below that value. $Mn_xZn_{1-x}Fe_2O_4$ ferrites are among the most temperature sensitive mixed ferrites and are used to prepare magnetic fluids in polar and non-polar solvents [2].

In turn, the fact that Gd-ferrite exhibits a Curie temperature as low as 298K and high pyromagnetic coefficient [4] could open the possibility to tune the T_c in Mn-Zn ferrites by a controlled incorporation of this rare-earth element into the ferrite structure. Tunability of Curie temperature would favor a further enhancement of the pressure gradient in the corresponding magnetocaloric system. Accordingly, the present work investigated the effect of composition on the corresponding magnetization and Curie temperature in Gd- and Eu-doped Mn-Zn ferrite nanocrystals. The effect of Eu-doping, another rare-

earth element with unpaired *4f* electrons, was also evaluated for comparison purposes.

2. EXPERIMENTAL

2.1 Materials

All reagents were of analytical grade and were used without further purification. Required weights of chloride salts of Fe, Zn, Mn, Gd and Eu ions were dissolved in distilled water to achieve a Fe/M, (M = Mn+Zn+Gd or Mn+Zn+Eu), mole ratio of two. NaOH was used as the alkaline precipitant.

2.2 Synthesis of Ferrite Nanocrystals

Mn-Zn ferrite nanocrystals were produced by conventional coprecipitation method. Aqueous solutions of 0.11 M Fe and 0.055M Mn-Zn was continuously added into the reaction vessel containing 0.725 M NaOH under boiling conditions and mechanically stirred at 500 rpm. A reaction time of four hours was long enough to permit the dehydration and atomic rearrangement involved with the conversion of the precursor hydroxide into the ferrite structure. Synthesized nanocrystals were removed out from solution, washed with deionized water and dried in air at 50°C.

2.3 Characterization

Structural analyses of the powders were carried out in a Siemens D5000 x-ray diffractometer (XRD) using the Cu-K α radiation. The particle morphology was examined by high-resolution transmission electron microscope (HRTEM). The magnetic properties of powders were measured in a SQUID unit. M-T curves were obtained under a maximum applied field of 7T.

3 RESULTS AND DISCUSSION.

3.1 XRD Analyses

Figure 1 shows the XRD patterns for Gd-doped $Mn_{0.8}Zn_{0.2}Gd_yFe_{2-y}O_4$ ferrites for a dopant atomic fraction, 'y', between 0.01 and 0.1. Similar patterns were observed for the Eu-doped ferrite. The excellent matching between the diffraction peaks of doped-ferrites with those corresponding to the undoped one, suggested that Gd^{3+} (ionic radii 0.97 Å) and Eu^{3+} (0.98 Å) can substitute Fe^{3+} ions (0.64 Å) in the host structure, at least in the evaluated range of dopant concentration. The average crystallite size, estimated by applying the Debye-Scherrer's equation for the (311) peak, varied between 6 and 9nm, when the fraction of Gd ions varied from 0.01 to 0.1. The corresponding lattice parameter, 'a', was slightly increased from 0.836nm to 0.838nm for 'y' 0.01 and 0.1, respectively. Despite the marked differences between ionic radius of dopants and iron ions, only a minor distortion in the unit cell was observed.

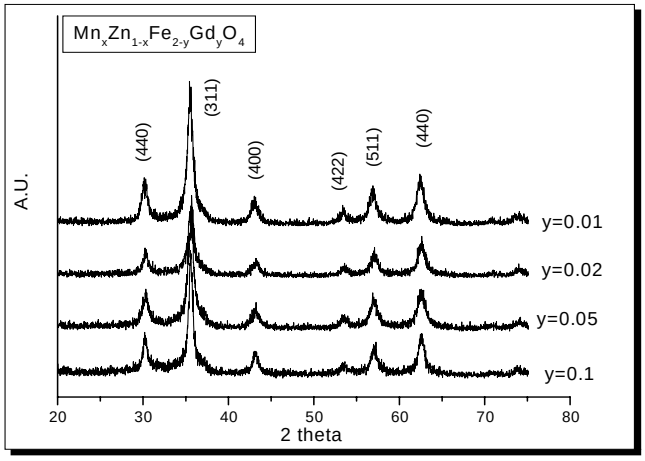

Fig. 1 XRD patterns for Gd-doped Mn-Zn ferrites synthesized at different Gd atomic fractions, 'y'.

3.2 HRTEM Analysis

HRTEM pictures of Figure 2 evidenced the nanocrystalline nature of the particles, which averaged 10nm in diameter. The picture corresponds to $Mn_{0.7}Zn_{0.3}Fe_2O_4$.

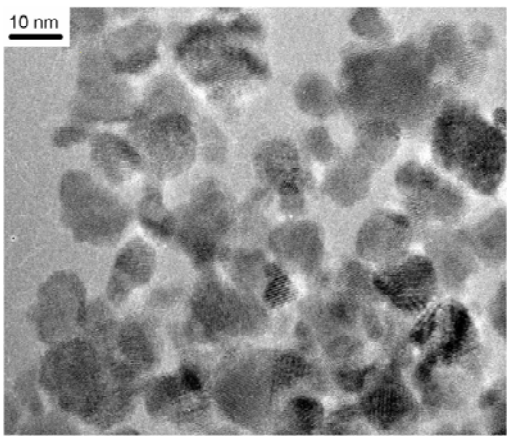

Fig. 2 HRTEM pictures of $Mn_{0.7}Zn_{0.3}Fe_2O_4$ nanocrystals.

3.3 Magnetic measurements

Figure 3 shows the room temperature M-H loops for $Mn_xZn_{1-x}Fe_2O_4$ nanocrystals synthesized at different Mn atomic fraction values, 'x'. As seen, the degree of magnetic saturation and the corresponding magnetization values were strongly dependent on the composition of the ferrites in the range evaluated. On the consideration that observed trends are exclusively related to compositions (i.e., no crystal size effects) the following rationale can be proposed.

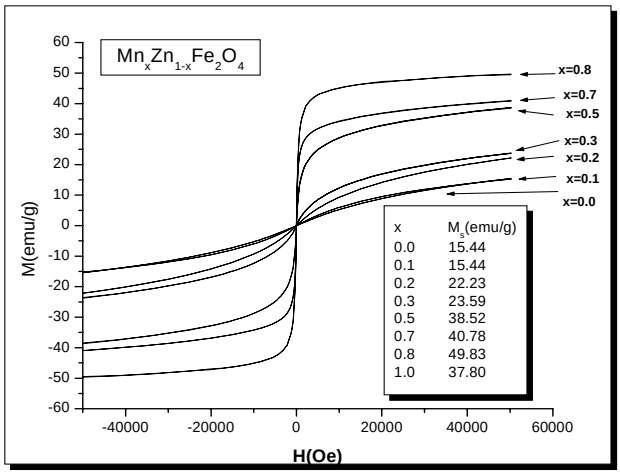

Fig. 3 Room temperature M-H loops for $Mn_xZn_{1-x}Fe_2O_4$ ferrites at different Mn atomic fractions, 'x'.

In Mn-Zn ferrites divalent and Fe^{3+} ions occupy both A- and B-sites in the ferrite structure, with Zn^{2+} preferring A-sites. The incorporation of magnetic Mn^{2+} for non-magnetic Zn^{2+} ions explains the observed enhancement in the maximum magnetization with a rising '*x*' value. For minor proportions of Mn^{2+} ions, i.e. low 'x' values, the ferrite becomes a normal spinel, i. e., no more Mn^{2+} in B-sites and no more Fe^{3+} in A-sites. This ionic redistribution can explain the observed drop in magnetization. In absence of Mn substitution ('x'= 0) a compensated anti-ferromagnetic behavior should be established in $ZnFe_2O_4$. Nevertheless, Figure 3 shows that even for x = 0 and 0.1, produced ferrites exhibited a small magnetization. It could be due to some inversion degree in the $ZnFe_2O_4$ structure where a small part of Zn^{2+} may still remain in B-sites and a part of Fe^{3+} in A-sites. The drop in magnetization observed for 'x' values above 0.8, could be attributed to the decrease in A-B type interactions in the $MnFe_2O_4$ structure ('x'= 1.0) in comparison with those interactions in the $Mn_xZn_{1-x}Fe_2O_4$ one.

Based on the above considerations, a ferrite with an atomic fraction of Mn ions of 0.8 was selected to investigate the effect of rare-earth doping on magnetic properties.

Figure 4 shows the M-H loops for Gd-doped Mn-Zn ferrites. The loop for the ferrite without Gd, i.e., 'y' = 0, is also included.

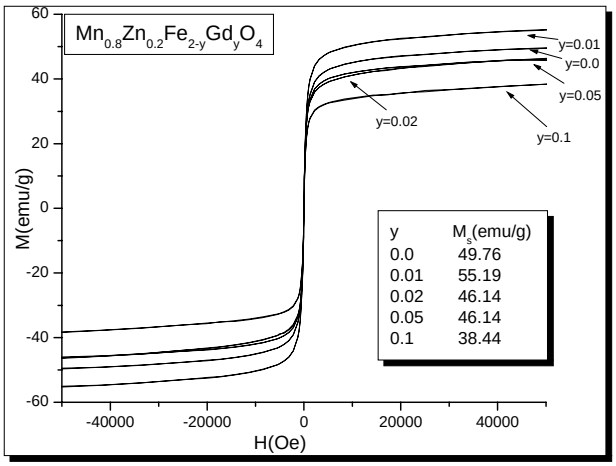

Fig. 4 Room temperature M-H loops for Gd-doped $Mn_{0.8}Zn_{0.2}Fe_2O_4$ ferrites at different Gd atomic fractions, 'y'.

As a general trend, the higher the Gd fraction in the Mn-Zn ferrite the lower the saturation magnetization. An exception was observed for 'y'= 0.01, where an increase in the maximum magnetization (55 emu/g) was observed with respect to the undoped ferrite, (49.8 emu/g). This rise in magnetization can be explained by substitution of Fe^{3+} by Gd^{3+} ions, having a higher magnetic moment, in B-sites. Upadhyay *et al.* [4] has attributed this variation in magnetization to the enhancing effect on the inter-sublattice exchange energy between Mn-O-Gd and Mn-O-Fe, with respect to the Fe-O-Fe interaction in the ferrite lattice. M-H measurements for the Eu-doped Mn-Zn ferrites revealed the drop in the maximum magnetization value Eu-atomic fraction varied from 0.01 to 0.1. The diminution in the average crystallite size of doped nanocrystals, determined from XRD measurements, could explain this behavior. Distortion of the ferrite structure by the incorporation of dopants -with ionic radios larger than host iron ions- could also be related with the drop in magnetization.

M-T data for Gd- and Eu-doped $Mn_{0.8}Zn_{0.2}Fe_2O_4$ are shown in Figures 5 and 6, respectively. T_c values, estimated by extrapolating the M-T plot, evidenced the dependence of this parameter with the concentration of the dopants. In the case of the ferrite

doped with Gd ('y'= 0.01), the rise in magnetization was conducive to an increase in the corresponding T_c value in comparison with the undoped sample.

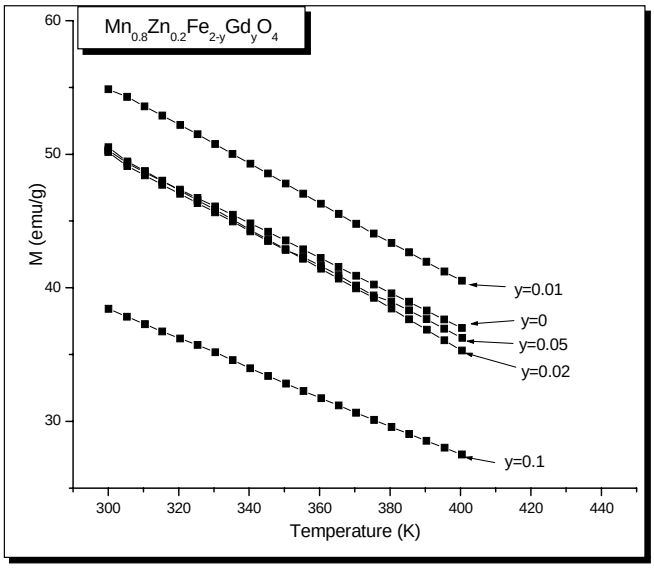

Fig. 5 M-T plots for $Mn_{0.8}Zn_{0.2}Fe_{2-y}Gd_yO_4$ ferrites at different Gd atomic fractions, 'y'.

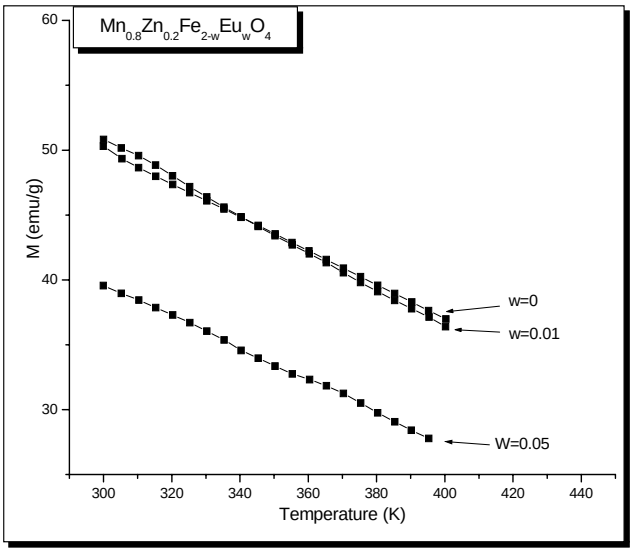

Fig. 6 M-T plots for $Mn_{0.8}Zn_{0.2}Fe_{2-w}Eu_wO_4$ ferrites at different Eu atomic fractions, 'w'.

The corresponding T_c values were 680K and 660K, respectively. T_c went down to 630K for y = 0.1. In the case of Eu-doped ferrites, the corresponding T_c values decreased continuously from 660K to 630K when the dopant atomic fraction varied from 0 to 0.05. The dependence of the Curie temperature with the type and concentration of the rare-earth dopant can be attributed to the above discussed effects of Fe substitution by Gd or Eu ions; although variations in the anisotropy constant of host Mn-Zn ferrites can also be considered [4]. Presented data suggested the feasibility in tuning the Curie temperature in nanocrystalline Mn-Zn ferrites by suitable selection of the type and amount of dopant species.

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References

[1] Rosensweig, R. E., Ferrohydrodynamics, Dover, New York (1997).

[2] Love, L. J., Jansen, J. F, Mcknight, T. E, Roh, Y. and Phelps, T. J. "A magnetocaloric pump for microfluidic applications", *IEEE Trans. Nanobioscience*, vol 3, n 2, 2004, pp.101-110.

[3] Odenbach S., "Recent progress in magnetic fluid research", *J. Phys.: Cond. Mat.*, 2004, pp. 1135-1149.

[4] Upadhyay R. V., Mehta R. V., Parekh K., Srinivas D. and Pant R. P. "Gd-substituted ferrite ferrofluid: a possible candidate to enhance pyromagnetic coefficient". *J. Magn. Magn. Mat.*, 201, 1999 pp. 129-132.