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Magnetic Enhancement in MnZn Nanoferrites Fabricated under a Magnetic Field

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Abstract: In a dc magnetic field of 6 T, $\text{Mn}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ nanoparticles are synthesized by a phase transformation method, and their structural and magnetic properties are investigated. Magnetic investigation displays the magnetic field enhances its saturation magnetization and decreases its magnetic loss. The magnetic field has effects on grain size and ion distribution, which causes high magnetization and low loss in MnZn nanoferrites.

Keywords: High Magnetic field; Nanoferrites; Soft-magnetic materials; MnZn ferrite; Structure; Magnetic properties

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Introduction

Good soft-magnetic materials exhibit a high magnetic permeability, a high saturation induction and a low coercivity. Moreover, they have a narrow hysteresis loop, low magnetic losses, and low eddy-current losses. MnZn ferrites are important to industry because of their good dielectric and magnetic properties, like high initial magnetic permeability, high electrical conductivity, and low magnetic loss [1,2]. To save energy and achieve device miniaturization, high saturation magnetization (M_s) is also one of major requirements for magnetically soft materials, because initial magnetic permeability is proportional to M_s square and coercivity is inversely proportional to M_s . Unfortunately, MnZn ferrites generally have low saturation magnetization due to their ferrimagnetism. To enhance the saturation magnetization, ion-substitution is conventionally applied in preparation of MnZn ferrites. However, the enhancement is limited [3]. In our previous papers [4,5], magnetic field has proved to be a powerful tool to

produce aligned compounds in composites, and control the phase transformation and behavior of the materials during transition processes, resulting in major improvements in material properties.

In this work, a phase transformation method under high magnetic field to synthesize nanocrystalline $\text{Mn}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ particles is developed. Compared with that of the sample fabricated under 0 T, M_s of the sample fabricated under 6 T is enhanced and the magnetic loss decreased. A method to improve M_s and to decrease loss of nanocrystalline MnZn ferrites is thus given.

Experimental details

Nanocrystalline MnZn ferrite particles were synthesized by a phase transformation method. The starting materials were high-purity $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2$, and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. According to the formula of $\text{Mn}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$, each starting material was weighted, and then added into 1 L de-ionized water

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with concentration of 1.538 M, stirring to complete dissolution. Precipitation and formation of nanoferrites took place by the conversion of metal salts into hydroxides, which occurred immediately, and followed by transformation of hydroxides into ferrites. Note that these processes were done in a quartz tube placed between two poles of the magnet. The intensity of the magnetic field between poles of the magnet can be adjusted. Under 0 and 6 T, the solutions were mixed together by stirring, then heated to the reaction temperature of 368 K, and aerated uniformly by pumping N_2 through porous glass to promote an oxidation reaction for 4 h. During oxidation, a small amount of NaOH solution was continuously added to keep the pH value at 9.5. The precipitated particles were washed, filtered and dried at 353 K after 4h reaction. The particle size and shape were characterized by transmission electron microscopy (TEM). Magnetic measurements were performed by using a physical properties measurement system (PPMS/Quantum Design).

Results and discussion

Figure 1 shows the TEM images of the particles under the magnetic field of 0 and 6 T, respectively. As shown in Fig. 2(a), the particles are relatively small,

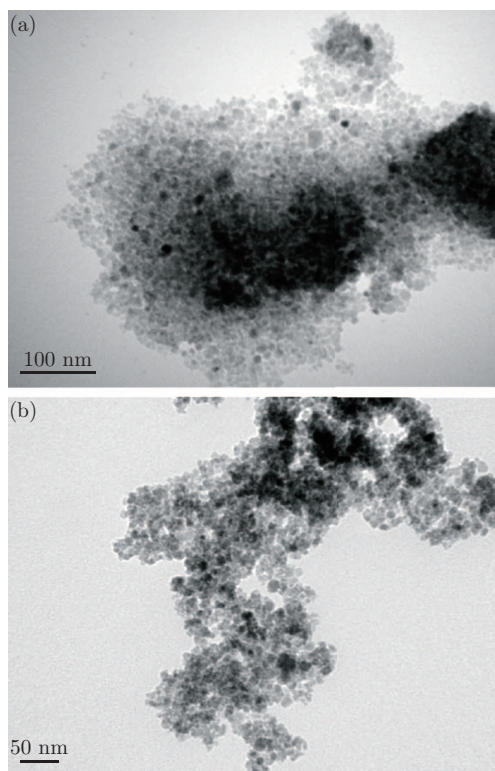


Fig. 1 Transmission electron microscopy images of the particles which precipitated under the magnetic field of (a) 0 and (b) 6 T, respectively.

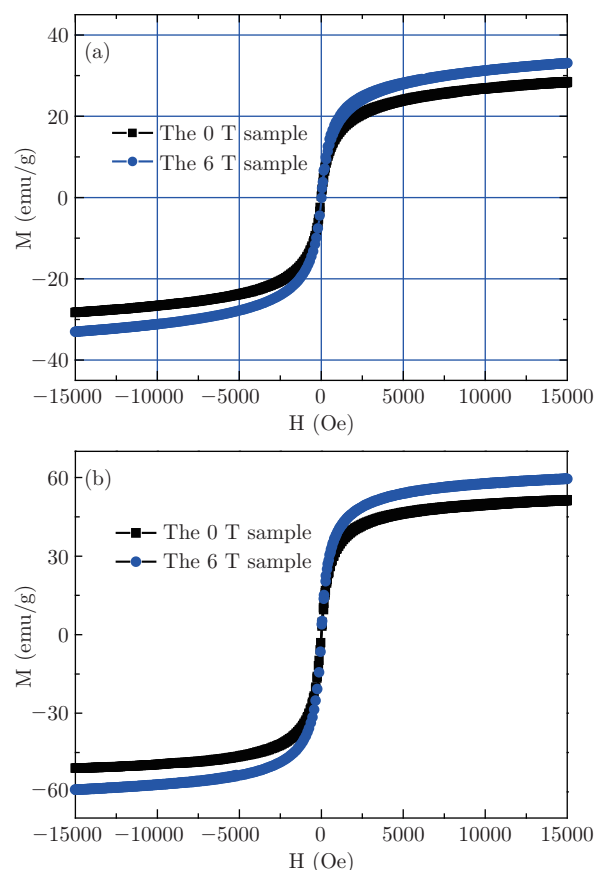


Fig. 2 (color online). Hysteresis loops of samples at (a) 300 K and (b) 120 K, respectively.

and the distribution of particle size is broad. With the increasing of magnetic field up to 6 T, however, the average particle size increases, and the particle size becomes uniform as shown in Fig. 2(b). The 6 T sample is consistent with the MnZn nano-ferrite particles by using a radio frequency induction plasma torch method [6]. When the magnetic field is applied to the system, the Gibbs chemical free energy of the MnZn ferrites decreases mainly due to the addition of a term of the order of magnitude of Zeeman energy ($-M \cdot H$, where M is the total magnetization of the sample and H the magnetic field) (the change in Gibbs chemical free energy of the non-magnetic parent is neglected here for simplicity). Therefore, the transition temperature under the magnetic field increases. On the other hand, the magnetic field suppresses the convection and the movement of matter by Lorentz force and magnetization force [7]. Hence, the reaction field can influence the grain/particle structure, size, shape, and crystallization. The two effects will increase nucleation and growth of MnZn ferrites, and, therefore, reduce the size distribution of the particles.

The 120 and 300 K magnetizations for applied magnetic field are shown in Fig. 2. Both the 0 T sample and the 6 T sample show hardly coercivity and remnance at 120 and 300 K. This is characteristic of superpara-

magnetism. In the single domain region, the coercivity decrease when the grain size is reduced, since the thermal energy can affect the alignment of magnetic moments inside the domain, characterizing superparamagnetic behavior. It is interesting that the magnetization of the 0 and 6 T samples are considerably different. At 120 K, the saturation magnetization values are ~ 51.2 and ~ 60.5 emu/g for the 0 and 6 T samples, respectively. At 300 K, the saturation magnetization values are ~ 28.5 and ~ 33.1 emu/g for the 0 and 6 T samples, respectively. The saturation magnetization of the 6 T sample is $\sim 18\%$ and $\sim 16\%$ higher than that of the 0 T sample at 120 K and 300 K, respectively. According to the theory of ferrimagnetism, the magnetization is the resultant of the unbalanced magnetisation of two ionic lattices with antiparallel alignment of their magnetic moments. MnZn ferrites have a spinel structure and show ferrimagnetic order below the Néel temperature. Their magnetic structure consists of two antiferromagnetically coupled sublattices. The Mn ferrites are 80% normal; this means that 80% of the Mn ions occupy the tetragonal *A* sites of the spinel AB_2O_4 structure, while the other 20% occupy the octahedral *B* sites. Zn ferrite is a normal spinel. Hence, A magnetic structure of $Mn_{0.6}Zn_{0.4}Fe_2O_4$ (the 0 T sample) is given by $(\vec{Mn}_{0.48}^{2+} \vec{Zn}_{0.4}^{2+} \vec{Fe}_{0.12}^{3+})_A [\vec{Mn}_{0.12}^{2+} \vec{Fe}_{1.88}^{3+}]_B O_4$. In spinel ferrites, the distribution of the ions on the *A* and *B* sites is determined by the total energy of the crystal, which depends on a number of factors such as the ion size, the Coulomb energy of the ions in the lattice. The difference in energy Δ between the normal and inverse spinel structure ranges from more than 1 eV to several hundreds of meV.⁸ In the case of a small Δ , a normal-inverse transition in magnetic structure can occur at a certain condition. Our nanoparticles have been fabricated by a magnetic-field-inducing technique and the ions in a high magnetic field are usually highly energetic. Thus, it is very likely that the material under high magnetic field is formed in conditions far from the thermodynamic equilibrium. As a result, one might expect ions to be randomly distributed among the *A* and *B* sites. The high magnetic field can cause Fe^{3+} transfer from the *A* site to the *B* site, and induce another magnetic structure $(\vec{Mn}_{0.48}^{2+} \vec{Zn}_{0.4}^{2+})_A [\vec{Mn}_{0.12}^{2+} \vec{Fe}_{2}^{3+}]_B O_4$. According to the magnetic structures, this would yield a magnetic moment $\sim 17\%$ larger than that of $(\vec{Mn}_{0.48}^{2+} \vec{Zn}_{0.4}^{2+} \vec{Fe}_{0.12}^{3+})_A [\vec{Mn}_{0.12}^{2+} \vec{Fe}_{1.88}^{3+}]_B O_4$, which is close to the experimental value obtained at 120 K.

Figure 3 gives the real component of a.c. susceptibility as a function of frequency (0~10000 Hz) for the 0 and 6 T samples. The imaginary component of both samples has similar change trend with frequency. The imaginary component of the 0 T sample is bigger than

that of the 6 T sample, and the higher the frequency is, the more considerable a difference of magnitude is. In a.c. susceptibility, the imaginary component indicates dissipative processes in the sample. Relaxation and irreversibility in spin-glasses give rise to a nonzero imaginary component. In ferri-magnets, a nonzero imaginary susceptibility indicates irreversible domain wall movement or absorption due to a permanent moment. So, it can be concluded that the 6 T sample has a lower loss than the 0 T sample, especially at high frequency, since the 6 T sample has a smaller imaginary susceptibility. This characteristic of the 6 T sample is very interesting in its high frequency use. As is well known, susceptibility is closely related to the magnetization behavior. The magnetization is created by domain wall movement and spin rotation, the relative contribution of each being a function of the frequency and the angle between the applied field and spin directions. In the present work, the magnetization is predominantly determined by the spin rotation, as the average grain size is small enough to be a single domain. According to Ref. 9, the magnetic properties of small grains depend strongly on the counterplay of local magnetic anisotropy energy and ferrimagnetic exchange energy. This implies that for the nanocrystalline Mn-Zn ferrite, ferrimagnetic exchange forces the magnetic moments to align parallel, thus preventing the magnetization from following the magneto-crystalline easy direction of each individual grain. Consequently, the effective anisotropy for the magnetic behavior is an average over several grains and, thus, reduced in magnitude.

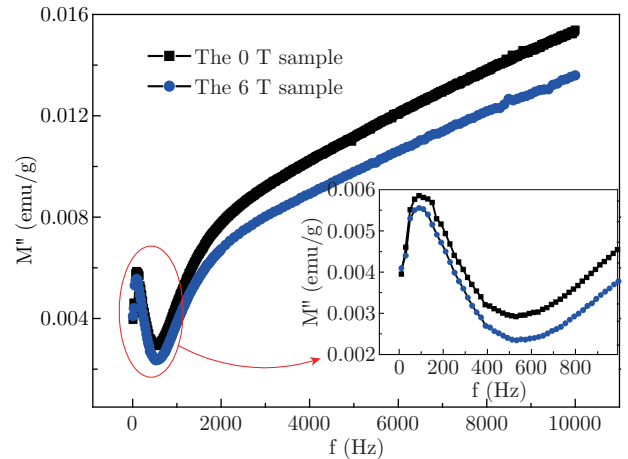


Fig. 3 (color online). The imaginary component of a.c. susceptibility as a function of frequency for the 0 and 6 T samples. The inset in Fig. 6 shows the enlarged region from 0 to 1000 Hz.

Conclusion

$Mn_{0.6}Zn_{0.4}Fe_2O_4$ particles are synthesized by a phase transformation method under different magnetic fields.

It is interesting that the saturation magnetization of the 6 T sample is $\sim 18\%$ and $\sim 16\%$ higher than that of the 0 T sample at 120 and 300 K, respectively. Magnetic investigation also displays the magnetic field decreases the magnetic loss. The magnetic field has effects on grain size, and ion distribution, which results from suppression of the convection and the movement of matter by the Lorentz force and the magnetization force. Considering that the saturation magnetization and magnetic loss are important parameters for soft magnetic materials, the technique promises to be an important approach in enhancing the saturation magnetization of nanoparticle ferrites.

Acknowledgments

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References

- [1] S. Calvin, E. Carpenter, B. Ravel, V. Harris and S. Morrison, *Phys. Rev. B* 66, 224405 (2002).
- [2] Q. Yan, R. Gambino, S. Sampath and Q. Huang, *J. Appl. Phys.* 97, 033902 (2005).
- [3] S. Chikazumi, *Physics of Ferromagnetism*, 2nd ed. (Clarendon, Oxford, 1997).
- [4] Y. Liu, J Zhang, S. Cao and Z. Ren, *J. Appl. Phys.* 104, 043901 (2008).
- [5] Y. Liu and J Zhang, et al, *Appl. Phys. Lett.* 94, 112507 (2009).
- [6] S. Son, R. Swaminathan and M. McHenry, *J. Appl. Phys.* 93, 7495 (2003).
- [7] X. Lu, A. Nagata, K. Watanabe, T. Nojima, K. Sugawara and S. Kamada, *IEEE Trans. Appl. Supercond.* 11, 3553 (2001).
- [8] A. Cormack, G. Lewis, S. Parker and C. Catlow, *J. Phys. Chem. Solids* 49, 53 (1988).
- [9] G. Herzer, *IEEE Trans. Magn.* 26, 1397 (1990).