JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 4, April 2007, p. 1158 - 1160

High magnetostrictive doped cobalt ferrite

O. CALTUN*, H. CHIRIAC[a], N. LUPU[a], I. DUMITRU, B. PARVATHEESWARA RAO[b]
Faculty of Physics, A.I. Cuza University, Iasi, 700506 Romania
[a]*The National Institute of R&D for Technical Physics, Iasi, 700050, Romania*
[b]*Department of Physics, Andhra University, Visakhapatnam 530003, India*

Manganese substituted cobalt ferrites have been shown to be promising candidate materials for stress and torsion sensor applications. In our study was investigated the influence of the manganese substitution on the magnetostrictive coefficient of ferrite samples with compositions of $CoFe_{2-x}Mn_xO_4$, where x ranges from 0 to 0.6. The samples were sintered for 5 hours in air at 1180 °C followed by natural cooling. The X ray analysis proves the existence of the spinel structure. Saturation magnetization, Curie temperature and magnetostriction measurements were performed on the samples to determine the influence of the substitution. The substitution of manganese for iron can decrease the Curie temperature and consequently the temperature of magnetomechanical effect. By modifying the manganese content and the sintering process, the material properties could be optimized for use in magnetomechanical stress sensors.

(Received January 25, 2007; accepted February 28, 2007)

Keywords: Co ferrite, Magnetostriction, Curie temperature, Magnetomechanical hysteresis, Sensors

1. Introduction

The magnetostrictive materials, having large applications, started to be, in the last decade, the subject of extensive research mainly due to three reasons. The first one: the industrial-scale preparation must be founded on the laboratory research. In the case of cobalt ferrites and of cobalt ferrite based composites it is important to clarify the conditions that determine the formation of some series of products showing high magnetostriction coefficients. The microstructure and the anisotropy induced during preparation or post-processing, the cation migration from tetrahedral to octahedral positions, the conduction mechanisms and, related to these, the catalytic properties need detailed analysis. The magnetization processes modelling, the study of the distribution of nano- and micro-particles coercitivity and of their interaction still has no coherent and congruent solutions. The second reason: the extension from the laboratory scale to industrial technology implies special problems of applied research. Magnetostriction properties of the cobalt ferrites obtained in laboratory indicates that they could be successfully applied in practice in several directions. As a massive material, they could be used as magnetic cores and force, pressure or torsion sensors. In the form of nano -powders, they can be used as catalysts or gas sensors in medicine, and as thin layers in nano and microelectronics. Practical applications could be restricted by some functioning parameters possibly controlled through technological processing parameters. The third reason: the industrial application is a complex field from the point of view of the competitive level. The new sensors compete on the market with others having already a good reputation. This is why the new product must be cheaper and better to overcome the users' suspicion on substitution of the old and known product with the new ones.

The previous studies have been shown that manganese substituted cobalt ferrites are excellent candidates for stress sensors due to a large magnetomechanical effect and high sensitivity to stress [1-3]. The magnetic anisotropy due to ordering in one direction is strongly related with cation distribution. Tailhades et al further demonstrated that a slow cooling of the cobalt ferrite samples promote directional ordering [4]. Jiles and his coworkers [5] have demonstrated that an increase the sintering temperature decreases the Curie temperature significantly from 500^{o}C to 450^{o}C. The fact that the Curie temperature and magnetostriction of substituted Co ferrite are tunable by adjusting the substitution levels allows the material properties to be optimized for use in magnetomechanical stress sensors over a range of operational temperatures.

2. Experimental details

Manganese-doped cobalt ferrite samples, with compositions of $CoMn_xFe_{2-x}O_4$, where x ranges from 0 to 0.6, were prepared, using standard powder ceramic technique, by substituting manganese for iron. The samples are denoted as follows P1 for x=0, P2 for x=0.2, P3 for x=0.3, P4 for x=0.4 and P5 for x=0.6. The raw materials of Fe_2O_3, MnO_2, and Co_3O_4 powders in targeted proportions were mixed and ball milled for 5 hours using the ball to powder ratio of 10:1 for sub micron particles. Then the resultant powders all the samples were calcined at 970°C for 4 hours in air atomosphere. The powder was again re-milled, mixed and granulated using 8% PVA, pressed into slugs, and sintered in air at 1180^{o}C for 4 hours and cooled in a furnace by switch off the furnace after the soaking temperature. The structural characterizations of the samples were done by X ray diffraction analysis and scanning electron microscopy. The magnetic properties were measured using vibrating sample magnetometry and built-in Curie temperature set-up, and magnetostriction coefficients were made using tensile strain gauge technique.

3. Results and discussions

The XRD analysis (Fig. 1) confirmed the spinel phase formation and all the samples demonstrate high crystalline structure. However, in the diffraction pattern of P2 sample a small residual phases of Fe_2O_3 and MnO_2 oxides were observed.

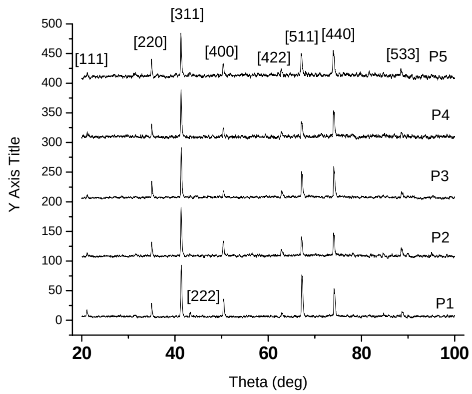

Fig. 1. XRD patterns.

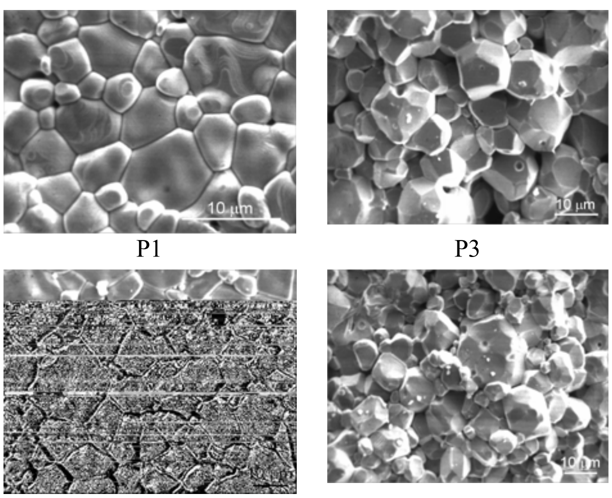

Fig. 2. SEM micrographs of $CoFe_{2-x}Mn_xO_4$ samples

The microstructures of the samples were characterized by scanning electron microscopy. Fig. 1 shows the microstructure of the P1, P2, P3 and P5 samples for comparison. The microstructure of the as sintered samples, as shows Fig. 2a for sample P1, is uniform with grains shaped in rounded regular forms. At low level of the manganese substitution (P1, P2) the density of the intergranular pores decrease and microstructure becomes uniform. The microstructures of the samples were uniform without pores on the surface and to the grain boundaries. Further increase of the substitution levels (P3, P5) decreases the average grain size but the density of the intergranular pores becomes higher as is showed in Fig 2b. However, for the whole range of the doping level, the average grain size variation is limited to a few micrometers only.

The studies of Jiles et al [5] demonstrated that by increasing the sintering temperature the Curie temperature significantly decreases from 500°C to 450°C. This is accompanied by the decrease of the temperature of the magnetomechanical hysteresis. The Curie temperature measurement have demonstrated in our samples case a decrease from 525°C for P1 to 355°C for P5 (Table 1). The decrease of the Curie temperature by substitution of iron ions by manganese suggests that manganese substituted cobalt ferrites could be used for obtaining some force, pressure and torsion sensors.

Table 1. Doping level, average grain size, Curie temperature, coercive magnetic field, saturation magnetization and magnetostriction coefficient data of $CoMn_xFe_{2-x}O_4$.

Sample	X %wt	D (µm)	Tc (°C)	Hc (Oe)	Ms (emu/g)	λ (-10^{-6})
P1	0	5.3	525	109	93	167
P2	0.2	7.8	495	63	102	50
P3	0.3	12.3	480	108	96	144
P4	0.4	7.3	418	68	95	119
P5	0.6	6.9	355	45	77	73

To understand the influence of the manganese substitution level on the magnetic properties of substituted Co ferrites the VSM measurement was done on the powders and as sintered samples. In order to discern whether the sintering process induced any magnetic anisotropy, the VSM measurements on bulk samples were done in two perpendicular directions, respectively to the direction of pressing direction. As can be seen from Fig. 2, the sintering process has not induced any magnetomechanical anisotropy. The VSM measurements for powders have demonstrated the influence of manganese substitution on saturation magnetization and coercive field of manganese substituted cobalt ferrites. The sample P2 is an exception from the rule of linear decrease of saturation magnetization [5]. The explanation could be the higher content of residual phases. The coercive filed decreases when increasing the manganese substitution level.

The variation of the saturation magnetization, Ms, depends on the cation distribution in a spinel lattice. Despite the decrease of the Curie temperature and strength of exchange interactions, the magnetization values for samples P2 and P4 have high values. This could be understood as due to contributions of a small number of $Mn2^+$ ions in the midst of $Mn3^+$ ions in B-sites resulting in larger B-sublattice magnetic contribution to the magnetization. Further increase in doping levels decreases the strength of the exchange interactions, as result the lower value of the saturation magnetization is expected

(P5). Chemical analysis and Mössbauer study on these samples would however help confirmation of the valence and site occupancy of Mn ions.

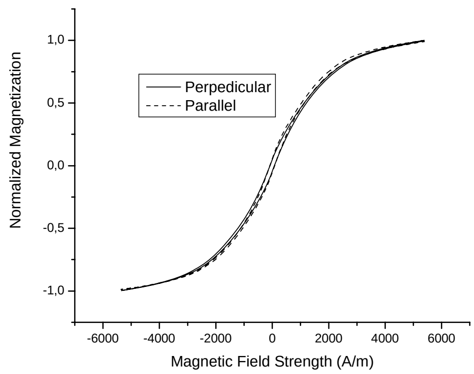

Fig. 3. Normalized hysteresis loop perpendicular and parallel to pressing direction for $CoFe_{1.8}Mn_{0.2}O_4$ sample.

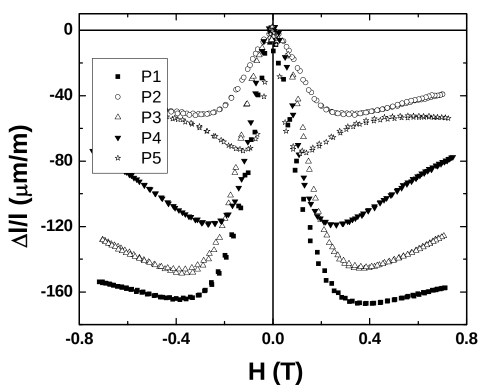

Fig. 4. Curves for all $CoMn_xFe_{2-x}O_4$ samples under the magnetostriction test.

The magnetostriction measurement was done under repeatedly tests and the average data are presented in Fig. 4. The samples without low Mn contents (P3) has maximum magnetostriction comparable with that of pure cobalt ferrite (P1). Further increase in manganese content (P4, P5) reduced the magnetostriction as in the previous study [3]. The sample P2 characterized by some residual phase is out range. The magnetostriction coefficient values are comparable with the values reported by earlier works on Mn substituted cobalt ferrites [4,5]. From this data we can conclude that residual phase compromise the magnetomechanical properties of Co ferrites and the application in producing sensors for automotive application. Low manganese substitution level increases the slope of the magnetostriction curve (dλ/dH) at low field. The slope of the magnetostriction curve is related to the stress sensitivity of the magnetization [6], and is an indication of potential performance of a magnetomechanical sensor based on cobalt ferrite.

4. Conclusions

The influence of manganese substitution level on the microstructure, magnetic and magnetomechanical parameters of cobalt ferrite were studied. The Curie temperature of cobalt ferrite can be reduced drastically by the substitution of Mn for Fe. The temperature dependence of magnetic and magnetomechanical properties can be refined by doping level in order to control the magnetostriction coefficient and the stability of the magnetomechanical properties. Decreasing the Curie temperature stress or torsion sensors operating at ambient temperature can be designed.

Acknowledgments

This research was supported by the Ministry of Education and Research of Romania under the Grant CEEX - MAGSAT and by ReCAMM, Korea.

References

[1] S. S. Shinde, K. M. Jadhav, J. Mater. Sci. Lett., **17,** 849 (1998).
[2] J. A. Paulsen, C. C. H. Lo, J. E. Snyder, A. P. Ring, L. L. Jones, D. C. Jile, IEEE Trans. Magn. **39,** 3316 (2003).
[3] J. A. Paulsen, A. P. Ring, C. C. H. Loa, J. E. Snyder, D. C. Jiles, J. Appl. Phys., **97** 044502 (2005).
[4] P. Tailhades, P. Mollard, A. Rousset, M. Gougeon IEEE Trans. on Magn. **26** (5) 1822 (1990)
[5] J. A. Paulsen, C. C. H. Lo, J. E. Snyder, A. P. Ring, L. L. Jones, D. C. Jiles, IEEE Trans. on Magn. **39**(5), 3316 (2003)
[6] Y. Chen, B. K. Kriegermeier-Sutton, J. E. Snyder, K. W. Dennis, R. W. McCallum, D. C. Jiles, J. Magn. Magn. Mater. **236**, 131 (2001).

*Corresponding author: caltun@uaic.ro