UDK 537.622:621.318.1
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 47(1)59(2013)

STRUCTURAL AND MAGNETIC PROPERTIES OF CERIUM-DOPED YTTRIUM-IRON GARNET THIN FILMS PREPARED ON DIFFERENT SUBSTRATES USING THE SOL-GEL PROCESS

STRUKTURNE IN MAGNETNE LASTNOSTI S CERIJEM DOPIRANE ITRIJ-ŽELEZOVE GARNETNE TANKE PLASTI, IZDELANE S SOL-GEL POSTOPKOM NA RAZLIČNIH PODLAGAH

Yavuz Öztürk[1], Mustafa Erol[2], Erdal Çelik[2,3], Ömer Mermer[1,3], Gökalp Kahraman[1], Ibrahim Avgın[1]

[1]Ege University, Dept. of Electrical and Electronics Engineering, Bornova, 35100 Izmir, Turkey
[2]Dokuz Eylul University, Dept. of Metallurgical and Materials Engineering, Buca, 35160 Izmir, Turkey
[3]Dokuz Eylul University, Center for Production and Applications of Electronic Materials (EMUM), Buca, 35160 Izmir, Turkey
yavuzoz@hotmail.com

Prejem rokopisa – received: 2012-07-13; sprejem za objavo – accepted for publication: 2012-08-27

The cerium-substituted yttrium-iron garnet (Ce-YIG) $Ce_xY_{3-x}Fe_5O_{12}$ is considered as a promising material for applications in high-performance magnetic and magneto-optic devices. In this work cerium-substituted yttrium-iron garnet films were produced on fused silica and Si(100) substrates using the sol-gel technique from solutions with the yttrium/cerium molar ratio 2.8/0.2. A heat treatment was applied to those as-deposited garnet films at temperatures ranging from 800 °C to 1000 °C for 2 h in air. The as-deposited garnet films were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) to investigate their structural properties. A vibrating-sample magnetometer was used at room temperature to characterize the magnetic properties of the as-deposited garnet thin films.

Keywords: sol-gel, yttrium-iron garnet, magnetic properties

S cerijem nadomeščen itrij-železov garnet (Ce-YIG, $Ce_xY_{3-x}Fe_5O_{12}$) je obetajoč material za uporabo v visoko zmogljivih magnetnih in magnetnooptičnih napravah. V tem delu je bila izdelana s cerijem nadomeščena itrij-železova garnetna tanka plast na kremenovem steklu in podlagi Si(100) z uporabo sol-gel tehnike iz raztopine z molskim razmerjem itrij/cerij 2,8/0,2. Nanesena garnetna plast je bila 2 h toplotno obdelana na zraku v temperaturnem območju od 800 °C do 1000 °C. Te plasti so bile karakterizirane z rentgensko difrakcijo (XRD), njihove strukturne značilnosti pa so bile pregledane z vrstičnim elektronskim mikroskopom (SEM). Vibracijski magnetometer je bil uporabljen pri sobni temperaturi za ovrednotenje magnetnih lastnosti nanesenih tankih garnetnih plasti.

Ključne besede: sol-gel, itrij-železo garnet, magnetne lastnosti

1 INTRODUCTION

Pure YIG films and their substituted derivatives have been researched for decades because of their wide range of applications in the microwave, communication and magnetic detection areas[1–3]. For instance, YIG is known to be one of the important ferrites in 1–2 GHz microwave applications owing to its small FMR line width[4]. However, the integration of garnets into semiconductor electronics is not straightforward as this process requires the garnet materials to be in nano/micro-sized dimensions. The magnetic and magneto-optical properties of YIG thin films will be affected by some parameters, namely, the type of the substituted material, the synthesis methods, the substrate and the structure/microstructure of YIG films[5–9].

YIG is the most representative and well-known compound among the rare-earth iron garnets. The definite composition and the presence of only trivalent metal ions make YIG particularly suitable for magnetic studies. There are eight formula units, $Y_3Fe_2(FeO_4)_3$, in a unit cell with a lattice constant $a = (1.2376 \pm 0.0004)$ nm. Some magnetic properties, such as magnetization, remanence, coercivity, Faraday rotation depend critically on the structure and the microstructure of the materials. Also, it is well known that deviations from stoichiometry have a strong influence on the magnetic properties of ferrites. There are three sub-lattices: tetrahedral (d), octahedral (a) and dodecahedral (c) in YIG and they are surrounded by four, six and eight oxygen ions, respectively. Among the five iron ions, which represent a formula unit, three are in 16 octahedral sites and two are in 24 tetrahedral sites[10]. A magnetic moment of 4.64×10^{-24} J/T per formula unit results from anti-ferromagnetic super-exchange interaction between the Fe^{3+} ions in these two different sites through the intervening O^{2-} ions. This corresponds to the moment of the one Fe^{3+} ion that is present at a tetrahedral site in numbers greater than the Fe^{3+} ions at an octahedral site. YIGs are also of scientific importance because of the wide variety of magnetic properties that we can obtain when substituting Y by rare-earth metals or substituting Fe by other trivalent cations.

A variety of techniques have been applied to obtain YIG thin films, such as radio-frequency (RF) sputtering, liquid-phase epitaxial (LPE) growth and pulsed-laser deposition (PLD). Most of these methods are generally vacuum type and expensive. Aside from vacuum-type expensive techniques, different wet chemical methods have been used to obtain the YIG structure, such as sol-gel, co-precipitation, micro-emulsion synthesis, citrate gel routes, hydrothermal synthesis, etc.[4–8]. In related researches, production processes usually focused on obtaining powder and bulk materials instead of producing thin films. Powder or bulk ceramic production techniques require high annealing temperatures and long processing duration, as mentioned in ref[11]. Materials that were used as components of electronic, magneto-optic or magnetic devices are all physically based on the movement of ions, the interaction of light and the change of the orientation in the structure. These structural properties change negatively with increasing material thickness or volume. In this way, producing thin films instead of thick films (coatings) or bulk materials will provide low annealing temperatures and a controlled structure. To the best of our knowledge, there are few studies on obtaining YIG thin films with chemical methods[4–8,12]. Unlike obtaining powder, producing thin films can be achieved at relatively low temperatures, like 700–1000 °C using the sol-gel method as a wet chemical route[8]. Nevertheless, it has been proved that the sol-gel process offers considerable advantages, such as better mixing of the starting materials and excellent chemical homogeneity in the final product. Moreover, the molecular level mixing and the tendency of partially hydrolyzed species to form extended networks facilitate the structure evolution, thereby lowering the crystallization temperature[13,14].

In this study, $Ce_xY_{3-x}Fe_5O_{12}$ thin films were successfully deposited from solution with a Y/Ce molar ratio of 2.8/0.2 on Si(100) and fused silica substrates through the sol-gel method from solutions that were synthesized with ethylhexanoate and 2,4-pentanedionate based precursors.

2 EXPERIMENTAL DETAILS

The precursor materials Fe 2,4-pentanedionate (0.1766 mg), Yttrium 2-Ethylhexanoate (0.1452 mg) and Ce 2-Ethylehexonate (0.01140 mg), were dissolved in methanol and glacial acetic acid (GAA) in order to form a 0.23-M solution with the chemical composition Ce : Y : Fe = 0.2 : 2.8 : 5. Three different solutions (A, B and C) with different methanol and GAA ratios were prepared as listed in **Table 1**. **Table 1** also shows the pH values of the solutions. In this study, GAA acts as a chelating agent to involve a homogenous solution. A higher GAA concentration leads to a poor interaction with the substrate and a lower GAA concentration leads to poorly dissolved precursors in a manner of the macro view. As a result, solution B was determined to be appropriate for deposition on substrates, since it has good wetting and chelating properties. The prepared optimal solutions were dip-coated on the fused silica and Si(100) substrates at room temperature in air. The gel films were dried at 300 °C for 10 min, and consequently heat treated in the range 800–1000 °C for 2 h in air in an electrical furnace. After this procedure, the specimens were cooled down from the annealing temperatures.

Table 1: Solvent – Chelating agent contents and pH values of the solutions A, B and C
Tabela 1: Vsebnost in pH vrednost raztopin topilo – kelat, A, B in C

Solution	Methanol (ml)	GAA (ml)	pH
A	2	1.5	3.6
B	2.5	1	3.05
C	3	0.5	2.5

X-ray diffraction (XRD, Rigaku D/MAX-2200/PC) patterns of the films were determined to identify the phase structure. The surface properties and topographies of the films were examined using scanning electron microscopy (SEM, JEOL JSM 6060) with attached energy-dispersive spectroscopy (EDS). The magnetic properties of samples were determined with a vibrating-sample magnetometer (VSM, Lakeshore 736, 7400) at room temperature.

3 RESULTS AND DISCUSSION

XRD patterns of selected samples on Si(100) and fused silica substrates are depicted in **Figures 1** and **2** respectively. All the produced films contain cubic Ce-substituted YIG films. As reported in the literature[15–17], cubic YIG formation with other impurity phases such as Y_2O_3, $FeYO_3$ and Fe_2O_3 was generally observed at temperatures between 700 °C and 1100 °C. In the present research, neither Y_2O_3 nor $FeYO_3$ phase formations were observed in the YIG film on either

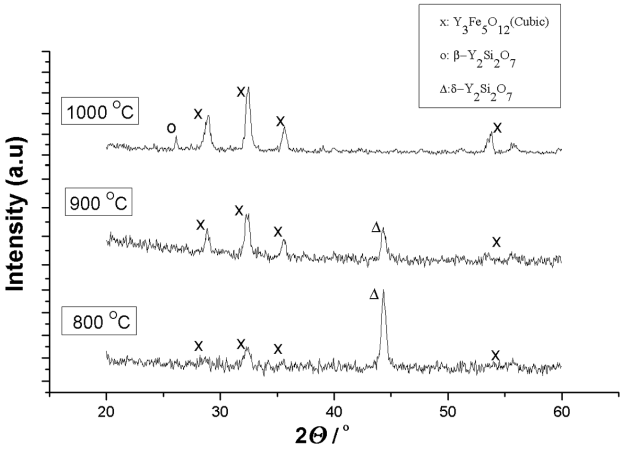

Figure 1: XRD patterns of Ce-YIG films coated on Si(100), annealed between 800 °C and 1000 °C for 2 h in air
Slika 1: XRD-posnetki Ce-YIG plasti na Si(100), žarjeni med 800 °C in 1000 °C, 2 h na zraku

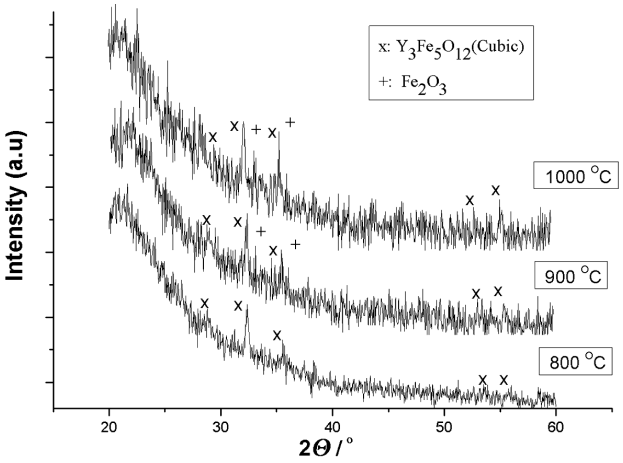

Figure 2: XRD patterns of Ce-YIG films coated on fused silica, annealed between 800 °C and 1000 °C for 2 h in air

Slika 2: XRD-posnetki Ce-YIG plasti na taljenem kremenu, žarjene med 800 °C in 1000 °C, 2 h na zraku

Si(100) or fused silica substrates. However, even though the Fe_2O_3 phase was found in the films on fused silica, it was not determined in the films on Si(100). At the same time, two different crystal structured yttrium silicate phases that transform from δ-$Y_2Si_2O_7$ to β-$Y_2Si_2O_7$ at 1000 °C were found. The formation of these silicate phases was considered to be substrate-film interactions. This formation and the increased annealing temperature affect the crystallization behaviour of the garnet in a positive way.

It is well known that the activation energy for nucleation is reduced by good lattice matching across the interface. As mentioned ref.[18] the nucleation mechanism depends on the substrates and denser nucleation was observed with an increasing lattice match. When the XRD results of the films on both substrates were compared, the Si substrates that were oriented exhibited better crystallization features than the amorphous fused silica. The different crystallization behavior observed for two substrates can be explained by the formation of silicate phases and differences in the nucleation mechanism. Furthermore, fused silica has a high resistance to chemicals, which reduces both interactions with the solution and silicate phase formation.

Sol-gel deposition is a wet chemical route in which the film quality is affected by various parameters such as substrate interaction, pH, humidity, and temperature. In order to tailor the magnetic and magneto-optical properties, film quality and homogeneity must be taken into consideration, as reported in refs[19,20]. The microstructural properties of Ce-YIG films were denoted in **Figure 3**. As can be seen from these micrographs, we have successfully obtained a coating of garnet structure with minor cracks. **Figure 3a** provides a general view of the structure of the films. In addition, some micro-size cracks structure can be seen on the magnified image, which is the result of the substrate film interaction, as shown in **Figure 3b**. The optimum thicknesses of the films were found to be around 300 nm using a profilometer. As far as magnetic properties are concerned, the magnetic hysteresis loop (M-H) of the Ce-YIG films on different substrates annealed at different temperatures was recorded with the VSM at room temperature. **Figures 4** and **5** diagrammatically clarifies the M-H loop of the Ce-YIG layers grown on the Si substrate annealed at

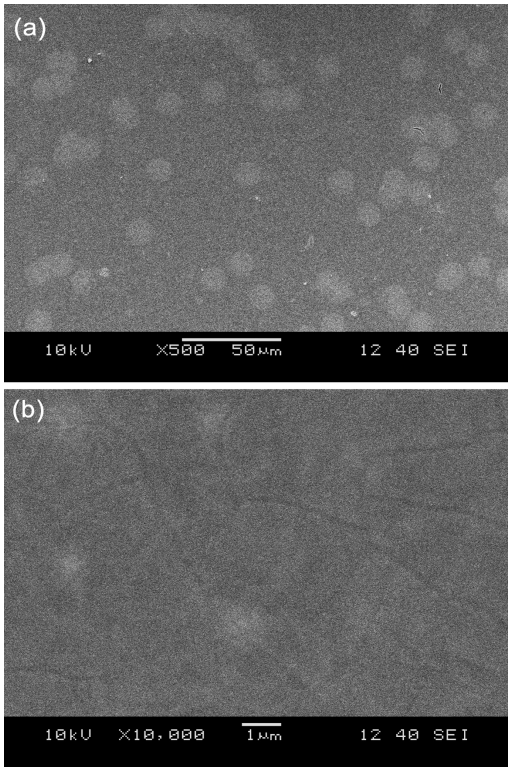

Figure 3: XRD SEM micrographs of Ce-YIG on Si(100) prepared at 1000 °C

Slika 3: XRD SEM-posnetka Ce-YIG na Si(100), pripravljenem pri 1000 °C

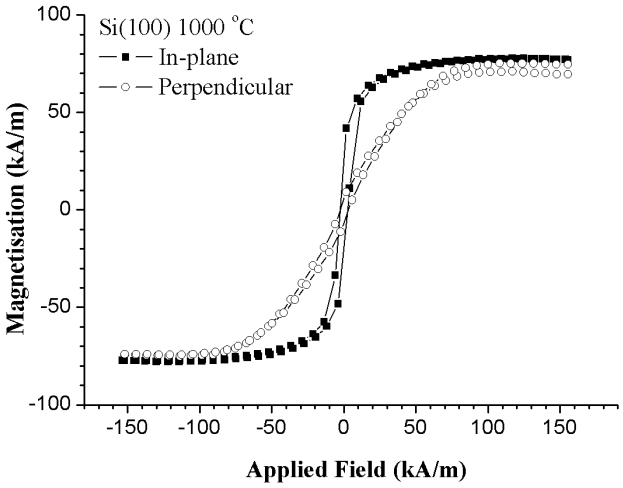

Figure 4: Magnetic hysteresis loops of Ce-YIG on Si(100) substrate annealed at 1000 °C

Slika 4: Magnetna histerezna zanka Ce-YIG na podlagi Si(100), žarjeno pri 1000 °C

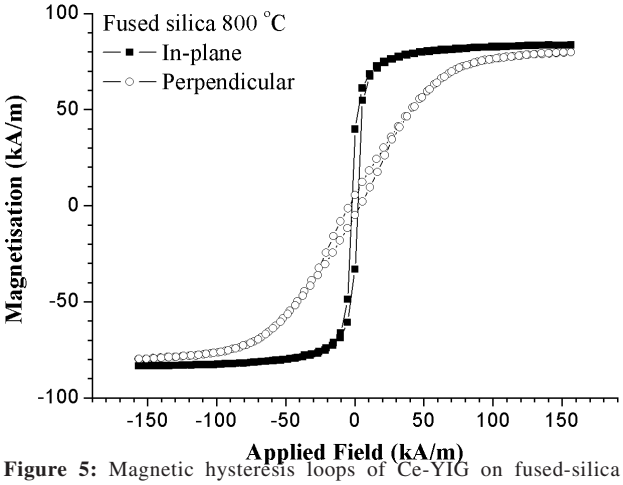

Figure 5: Magnetic hysteresis loops of Ce-YIG on fused-silica substrate annealed at 800 °C

Slika 5: Magnetna histerezna zanka Ce-YIG na taljenem kremenu, žarjeno pri 800 °C

1000 °C and 800 °C, respectively. The applied magnetic field (H_{ex}) is both in plane and perpendicular with respect to the Si wafer. Different annealing temperatures were also applied on the Ce-YIG film on Si and their M-H loops were also measured, but are not shown in the figure. All the parameters related to the magnetic properties of these films were summarized in **Table 2**. These results indicate that strong magnetic anisotropy has been detected for different annealing temperatures of the Ce-YIG films. As the annealing temperature increases, the coercivity values of the film decreases for a field perpendicular to the Si wafer but this does not change significantly for the in-plane field. The saturation magnetization values increase strongly as the annealing temperature increases. This shows that an increase of the annealing temperature changes the substrate–film interaction[21] and also increases the Ce-YIG phase with respect to the $Y_2Si_2O_7$ phases.

In order to compare the effect of different substrates on the magnetic properties, the Ce-YIG film was coated on fused silica. Again, all the films were annealed at the same temperature as that of the Ce-YIG on the Si substrate. **Figure 5** shows the M-H loop of Ce-YIG on fused silica annealed at 800 °C. The magnetic properties of these films for different annealing temperatures were also summarized in **Table 3**. As is evident from **Table 3**, increasing the annealing temperature does not change significantly the coercivity values for a field perpendicular to wafer; however, it decreases them for an in-plane field. For fused-silica substrates the saturation magnetization values decrease strongly when the annealing temperature increases. In this case decreasing the saturation magnetization is mainly due to the formation of the Fe_2O_3 phase in the films, as shown by the XRD pattern in **Figure 2**. This was also confirmed in our previous study[12].

A different range of magnetization values as compared to the bulk in garnet thin films have commonly been observed[21–23]. Lower values of the magnetization explained by parasitic phases in the structure or poorly crystallized and magnetically disordered grain-boundary materials[24]. A strong in-plane magnetic anisotropy was observed for the Ce-YIG films grown on both substrates, indicating that the substrate–film interaction has an important role in the formation of the crystalline structure as well as the magnetic properties. Because of the in-plane anisotropy, these kinds of films are useful for applications of planar waveguides and magnetic biasing.

4 CONCLUSIONS

Ce-substituted YIG thin films were synthesized on fused silica and Si(100) substrates with solutions prepared from Ce, Y, and Fe-based precursors. The microstructural (SEM) results indicate good surface quality with micro cracks. Also, two different crystallization

Table 2: Magnetic properties of Ce-YIG films on Si substrate at different annealing temperatures

Tabela 2: Magnetne lastnosti plasti Ce-YIG na Si-podlagi pri različnih temperaturah žarjenja

Substrate	Annealing temp. (°C)	Saturation Magnetization (kA/m)	Perpendicular		In-plane	
			Remanence (kA/m)	Coercivity (kA/m)	Remanence (kA/m)	Coercivity (kA/m)
Si(100)	800	33	4	4.856	11	2.070
Si(100)	900	51	4	3.185	15	2.070
Si(100)	1000	78	7	2.866	22	2.468

Table 3: Magnetic properties of Ce-YIG films on fused-silica substrate at different annealing temperatures

Tabela 3: Magnetne lastnosti plasti Ce-YIG na kremenovem steklu pri različnih temperaturah žarjenja

Substrate	Annealing temp. (°C)	Saturation Magnetization (kA/m)	Perpendicular		In-plane	
			Remanence (kA/m)	Coercivity (kA/m)	Remanence (kA/m)	Coercivity (kA/m)
Fused silica	800	83	7	4.299	41	2.229
Fused silica	900	49	6	4.936	28	2.627
Fused silica	1000	39	5	4.459	23	2.946

dynamics were observed for the two substrates. The YIG phase was obtained at 800 °C with the highest magnetization value (83 kA/m) in all the samples deposited on the fused-silica substrates. The Fe_2O_3 phase was obtained at higher annealing temperatures. For the Si(100) a strong substrate-layer interaction was observed, which causes yttrium silicate phases. Higher annealing temperatures led to a substrate-film interaction with higher crystallization and increased magnetization. All the films show strong in-plane anisotropy that would be suitable for waveguide- or magnetic-biasing-based devices.

Acknowledgement

This work was financially supported by the Scientific and Technological Research Council of Turkey (TUBITAK, project number 106T651).

5 REFERENCES

[1] S. Higuchi, Y. Furukawa, S. Takekawa, O. Kamada, K. Kitamura, K. Uyeda, Sens. Actuators A, 105 (**2003**), 293

[2] T. Shintaku, T. Uno, Jpn. J. Appl. Phys., 35 (**1996**), 4689

[3] K. Matsumoto, S. Sasaki, Y. Yamanobe, K. Yamaguchi, T. Fujii, Y. Asahara, J. Appl. Phys., 70 (**1991**), 1624

[4] V. G. Harris, A. Geiler, Y. Chen, S. D. Yoon, M. Wu, A. Yang, Z. Chen, P. He, P. V. Parimi, X. Zuo, C. E. Patton, M. Abe, O. Acher, C. Vittoria, J. Magn. Magn. Mater, 321 (**2009**), 2035

[5] P. Vaqueiro, M. P. Crosnier-Lopez, M. A. Lopez-Quintela, J. Solid State Chem., 126 (**1996**), 161

[6] X. Z. Guo, B. G. Ravi, P. S. Devi, J. C. Hanson, J. Margolies, R. J. Gambino, J. B. Parise, S. Sampath, J. Magn. Magn. Mater., 295 (**2005**), 145

[7] M. Inoue, T. Nishikawa, H. Otsu, H. Kominami, T. Inui, J. Am. Ceram. Soc., 80 (**1997**), 2157

[8] C. S. Kuroda, T. Taniyama, Y. Kitamoto, Y. Yamazaki, J. Magn. Magn. Mater., 241 (**2002**), 201

[9] K. Matsumoto, S. Yamamoto, Y. Yamanobe, A. Ueno, K. Yamaguchi, T. Fujii, Jpn. J. Appl. Phys., 30 (**1991**), 1696

[10] S. Geller, M. A. Gilleo, Acta Cryst, 10 (**1957**), 239

[11] Z. Abbas, M. Ramadan Al-habashi, K. Khalid, M. Maarof, Eur. J. Sci. Res., 36 (**2009**), 154

[12] Y. Ozturk, I. Avgın, M. Erol, E. Çelik, Advances in Nanoscale Magnetism, Springer Proceedings in Physics, 122 (**2009**), 113

[13] H. Xu, H. Yang, J. Mater. Sci.: Mater Electron, 19 (**2008**), 589

[14] H. Bahadur, A. K. Srivastava, R. K. Sharma, S. Chandra, Nanoscale Res. Lett., 2 (**2007**), 469

[15] X. Zhou, W. Cheng, F. Lin, X. Ma, W. Shi, Appl. Surf. Sci., 253 (**2006**), 2108

[16] Z. Wei, G. Cuijing, J. Rongjin, F. Caixiang, Z. Yanwei, Mater. Chem. Phys., 125 (**2011**), 646

[17] H. G. Beh, R. Irmawati, Y. Noorhana, K. P. Lim, IJET, 2 (**2009**), 261

[18] M. B. Park, N. H. Cho, J. Magn. Magn. Mater, 231 (**2001**), 253

[19] M. Xiangyang, S. Jian, S. Zhang, D. Que, J. Mater. Sci. Lett., 17 (**1998**), 1635

[20] M. Xiangyang, Z. Shouye, L. Fengzhen, Q. Duanlin, J. Mater. Sci. Mater. Electron, 9 (**1998**), 347

[21] K. H. Shin, M. Mizoguchi, M. Inoue, J. Magn., 12 (**2007**), 129

[22] A. C. Rastogi, V. N. Moothy, Mater. Sci. Eng. B, 95 (**2002**), 131–136

[23] N. Kumar, D. S. Misra, N. Venkataramani, S. Prasad, R. Krishnan, J. Magn. Magn. Mater., 276 (**2004**), 899

[24] E. Popova, N. Keller, F. Gendron, M. Guyot, M. C. Brianso, Y. Domond, M. Tessier, J. Appl. Phys., 90 (**2001**), 1422