Journal of Solid State Chemistry 181 (2008) 2123–2126

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Electromagnetic transport properties and magnetoresistance of $La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$– Ag composites prepared by electroless process

C.S. Xiong *, Y.F. Cui, Y.H. Xiong, H.L. Pi, X.C. Bao, Q.P. Huang, Y. Zeng, F.F. Wei, C.F. Zheng, J. Zhu

Department of Physics, Huazhong University of Science and Technology, Wuhan 430074, PR China

ARTICLE INFO

Article history:
Received 30 September 2007
Received in revised form
13 January 2008
Accepted 29 April 2008
Available online 14 May 2008

PACS:
75.47.Lx
61.72.Mm
75.60.Ch

Keywords:
Manganites
Grain boundary
Electroless plating process
Room temperature magnetoresistance

ABSTRACT

A series of bulk polycrystalline $La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$ (LCSMO)–Ag composites were prepared by electroless plating process and several kinds of physical properties have been studied systemically. According to the results of X-ray diffraction (XRD), scanning electron microscopy (SEM), and electromagnetic transport properties, we can see that Ag-added segregated at the surfaces or interfaces of LCSMO grains. The metal-insulator transition temperature (T_P) and Curie temperature (T_c) were almost unchanged but ρ decreased with increasing plating time. We also observed Ag-added can significantly enhance the magnetoresistance (MR) near T_P under a low applied field (3000 Oe) and the room temperature MR reached to 35% under 20 kOe, which is encouraging for practical applications. We can suggest that improved grain boundary effect by Ag-added is responsible for the enhancement.

1. Introduction

Perovskite manganites of the type $La_{1-x}A_xMnO_3$ ($A = $ Sr, Ca, Ba, or Pb) have triggered renewed interest since the discovery of the phenomenon of colossal magnetoresistance (CMR) in these compounds [1–4]. However, the intrinsic CMR effect in the perovskite manganites, which is caused by the double exchange (DE) mechanism [5,6], is usually found on a magnetic field scale of several Teslas and a narrow temperature range [7], which severely limits its practical applications. Therefore, it is highly desirable to develop low field magnetoresistance (LFMR) materials. Some attempts have been made to enhance the LFMR effect of perovskite manganites by mixture of the CMR materials with secondary insulator phases, such as LSMO–CeO_2 [8], LSMO–$CoFe_2O_4$ [9], LBMO–YSZ [10], LCMO–ZrO_2 [11], etc. However, the mixture of the CMR material with the insulating compound commonly results in large increase of resistivity and downshift of metal-insulator transition, especially the LFMR always appears at lower temperature while weakening the intrinsic MR, which limits the practical applications. If a conducting metal is introduced into the manganite matrices to form ferromagnet-metal-type compound, enhanced MR could also be expected. Among these conducting materials, silver is a suitable candidate [12–15]. Recent reports [12,15] have revealed that, adding Ag in polycrystalline film or bulk CMR compounds can obtain large room temperature MR if T_p of the compounds is near room temperature via improving the microstructure of the surfaces, electrical and magnetic inhomogeneities on the grains. Moreover, since the high conducting metal Ag provides conduction paths among grains, the resistivity of Ag-added manganites can be much lower.

Based on the above reasons, it encourages us to study the effect of nonmagnetic Ag addition into the ferromagnetic (FM) $La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$ (LCSMO) matrix. On the one hand, LCSMO is one of the well-studied CMR materials whose T_P is near room temperature. On the other hand, it is well known that the preparation condition can affect the microstructure and electromagnetic transport properties of the samples. In this paper, we have used an electroless plating method to introduce metal Ag into the LCSMO matrix. This method offers higher purity and produces better homogeneous systems, which can modify the grain boundaries and lead to the improvement of the properties. The modification of the grain boundaries is responsible for the enhancement of MR.

2. Experimental

The LCSMO/xAg (x is the plating time) samples with $x = 0, 3, 5, 8, 15, 20, 25, 30$, and 35 min were synthesized by three steps: First,

---

* Corresponding author. Fax: +86 27 87556914.
E-mail address: csxiong@mail.hust.edu.cn (C.S. Xiong).

0022-4596/$ - see front matter © 2008 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2008.04.041

the LCSMO powders were prepared by a conventional solid-state reaction method. High-purity powders of La_2O_3, $CaCO_3$, $SrCO_3$, and MnO_2 were mixed in stoichiometric proportions and ground for 8 h. Then the mixed powders were presintered in air at 800 °C for 10 h and ground for 2 h. At last, the LCSMO powders were sintered at 1400 °C for 10 h. Secondly, we introduced metal Ag into LCSMO matrix through the electroless plating process. The analytical reagents of $AgNO_3$ (0.34 g) and $C_4H_4O_6KNa \cdot 4H_2O$ (1.5 g) were dissolved in distilled water under magnetic stirring, respectively. $AgNO_3$ was served as a source of Ag, and $C_4H_4O_6KNa \cdot 4H_2O$ was a complexant. Under continuously magnetic stirring, $NH_3 \cdot H_2O$ (27%) was added dropwise to the $AgNO_3$ solution (3.4 g/L) to achieve a transparent uniform precursor solution with PH~9 adjusted with NaOH solution (9 g/L). Then $C_4H_4O_6KNa \cdot 4H_2O$ solution (15 g/L) was added to the precursor solution to form a uniform mixed solution (100 mL). After that, LCSMO powders (2 g) were dipped into this mixed solution. The Ag^+ was deoxidized into metal Ag and was deposited on the surfaces of LCSMO grains. The Ag content was controlled through different plating time. All the experiments were accomplished at room temperature. Then we separated the Ag-coating LCSMO powders from the solution by a magnet and flushed with distilled water twice. The wet powders were desiccated at about 100 °C for 1 h. Thirdly, the as-prepared composites were pressed into pellets at a pressure of 8 MPa and sintered in air at 1000 °C for 2 h and naturally furnace-cooled to room temperature. In this way, a series of LCSMO/*x*Ag composites were obtained.

The crystal structures of the samples were characterized by X-ray diffraction (XRD) with Cu*K*α radiation in the 2*θ* range from 20° to 80°. The morphology was examined by the scanning electron microscope (SEM). The magnetic measurements were done using a vibrating sample magnetometer in the temperature range from around 80 to 360 K in an applied field of 4000 Oe. The temperature dependence of the resistivity was measured using the standard DC four-probe method.

3. Results and discussion

Fig. 1 shows the XRD patterns of some representative samples with different silver-plating time. The pattern shows a single rhombohedral perovskite structure for the pure sample. With the increase of *x*, the XRD patterns consist of two sets of diffraction peaks: LCSMO and metal Ag, and the peak intensity of Ag increases. The result shows that the perovskite LCSMO and Ag-rich phases coexist in the present composites. On the one hand, considering the special experimental procedure, before mixed with Ag, a uniform LCSMO grain has been formed. Then, during the mixing process, the doped Ag is preferentially segregated at the surfaces of LCSMO grains. On the other hand, since the sintering time of the samples is only 2 h, the reaction between LCSMO and Ag is difficult in the special experimental procedure. Hence, we can assume that the metal Ag mainly homogeneously segregates at the surfaces of the LCSMO grains.

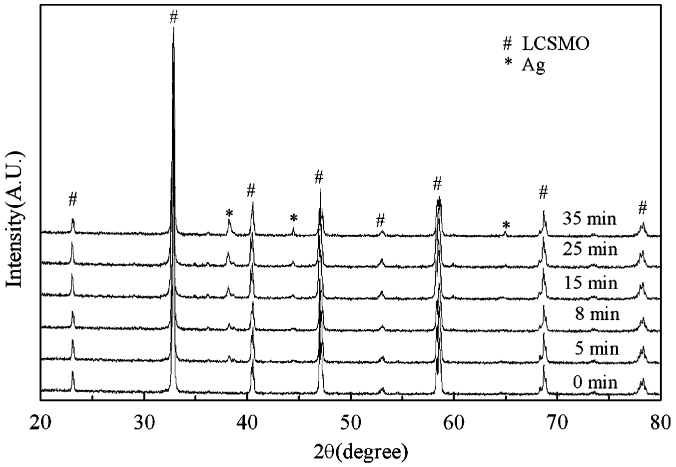

Fig. 1. The XRD patterns of representative LCSMO–Ag samples with different plating time.

In order to analyze the effects of Ag introduction on the microstructure of LCSMO grains and the distribution of Ag in the composites, the fracture sections of all the samples were examined by the SEM. Some selected samples' SEM micrographs are exhibited in Fig. 2. Fig 2(a) is pure LCSMO matrix. The sample without sintering with plating time for 10 min is shown in Fig 2(b). As one can see, the little Ag grains are deposited homogeneously on the surfaces of LCSMO grains, which is better than the conventional mechanical mixture of CMR materials with Ag [15]. Fig 2(c) is the sample sintered at 1000 °C for 2 h with the plating time of 10 min. The bright regions are metal Ag. The gray regions denote the LCSMO matrix. This gives further evidence that no chemical reaction takes place between LCSMO and Ag. Under our sintering conditions, we can assume Ag partly melted and entered the interstices of LCSMO grains. So we can conclude that Ag segregates at the surfaces or interfaces of LCSMO grains, which is in accordance with the conclusion from the XRD.

The temperature dependence (*T*) of the special magnetic moment (σ_S) measured at 4000 Oe for some selected composites and the results are shown in Fig. 3. As can be seen, the ferromagnetic (FM) to paramagnetic (PM) phase transition temperature (T_C) is independent of Ag content and is ~325 K for all samples. We can conclude that Ag entirely segregated at the surface or interface of LCSMO grains once more. The nonmagnetic Ag plays a role of dilution effect in the composites, so σ_S decreases monotonically with the increase of the plating time *x*.

Fig. 4 shows the temperature dependence of zero field resistivity for all samples measured at about 90–360 K. Results show that (1) for all samples, an intrinsic metal-insulator transition was observed at a temperature T_P, which results from the DE mechanism of LCSMO. This is also the origin of CMR. (2) The transition temperature T_P of all the Ag-doped LCSMO composites is almost unchanged compared with that of pure LCSMO. (3) Moreover, the resistivity (ρ) decreases with Ag addition.

On the basis of the special experimental procedure and the above analysis, we have known that the metal Ag segregated at the surfaces of the LCSMO grains. So, we think the grain boundary effect plays an important role in this system. The following is our explanation of the influences of Ag addition on LCSMO grains from two aspects: On the one hand, Ag entirely segregated at the grain boundaries or surfaces can improve the atomic disorder and magnetic inhomogeneity on the grain boundaries/surfaces caused by the coexistence of broken bonds and symmetry breaking. With the increase of Ag addition, homogeneity and crystallization of LCSMO are improved. Consequently, the barriers formed by the inhomogeneity on the grain boundaries/surfaces become thinner. So the electron scattering is suppressed and the tunneling probability is enhanced. On the other hand, the existence of high conductive metal Ag between the LCSMO grains opens a new conductive channel for the electron transport in the insulating regions. Especially, the composites were sintered at 1000 °C, which is higher than the melting point of Ag (960 °C), Ag is melted and thus dispersed into the interstice of the LCSMO grain and enhances the connectivity between the grains, which also induces the decrease of ρ.

It's believed that the presence of T_P of the Ag-doped composites should be indicative of the alignment of Mn spins

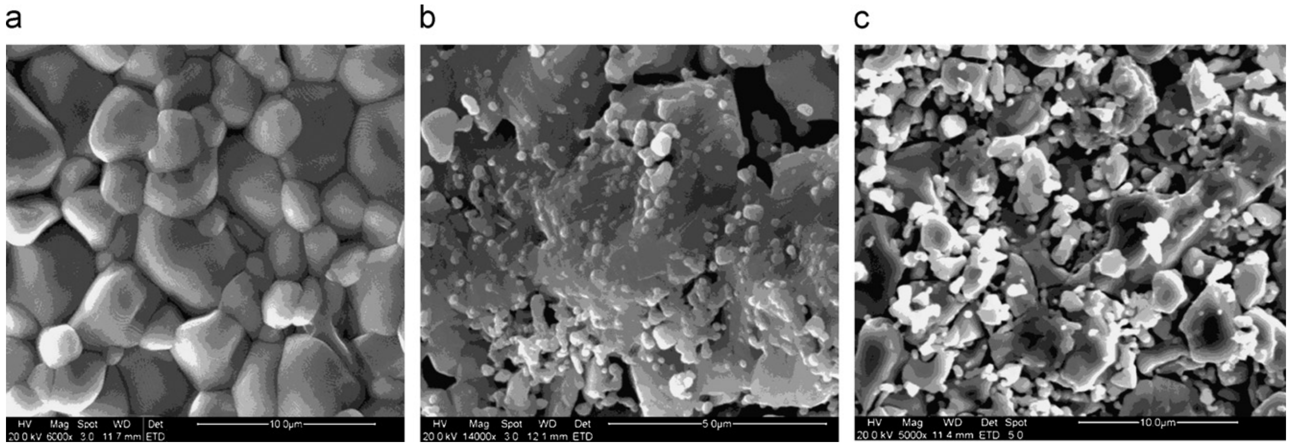

Fig. 2. The SEM images of LCSMO–Ag samples. The staff gauge is 10, 5, and 10 μm from left to right. (a) Is the pure LCSMO. (b, c) are the samples of plating time for 10 min without sintering and sintered at 1000 °C for 2 h, respectively. The bright pots are metal Ag for (c).

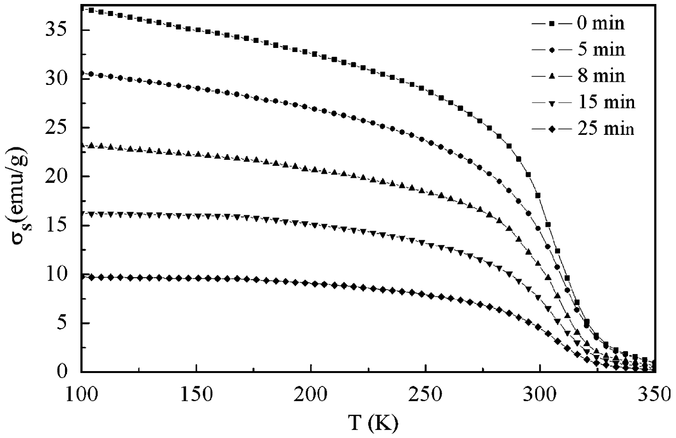

Fig. 3. The special magnetic moment (σ_S) versus temperature for some samples in the warming process, measured in 4000 Oe.

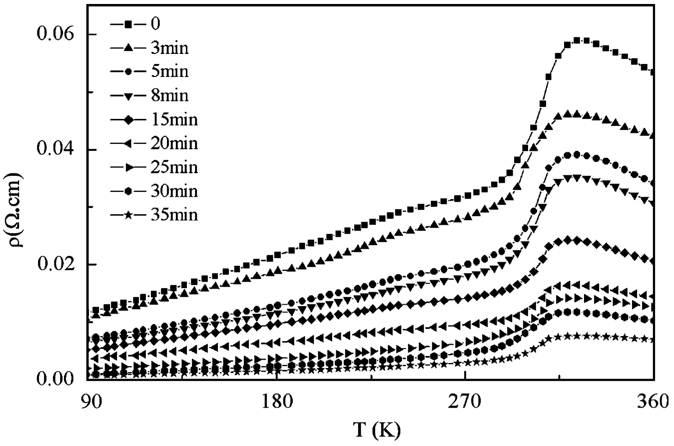

Fig. 4. Temperature dependence of resistivity for all LCSMO–Ag samples in zero field prepared by electroless plating with different plating time.

within the LCSMO grains similar to pure LCSMO. It is an intrinsic property of manganites, which is determined by the DE interaction [5,16]. For the LCSMO/*x*Ag composites, metal Ag does not enter the LCSMO lattice but just segregates at the interfaces or surfaces, which does not change the proportion of Mn^{3+} and Mn^{4+} ions and the oxygen content. As a result, T_P is not changed either.

Shown in Fig. 5 is the curves of the temperature dependence of the MR for the composites with $x = 0$, 8, 20, 25, 30, and 35 min in a field of 3000 Oe. Here MR is defined as MR (%) $= (\rho_0 - \rho_H)/\rho_0$, where ρ_0 and ρ_H are the resistivity values in zero and applied fields, respectively. It can be seen that the MR is obviously enhanced near T_P (312 K). With the increase of Ag content, the MR increases until a maximum ($x = 25$ min) and then decreases again ($x > 25$ min). The maximum MR is as large as 19%, almost 2.5 times larger than that of pure LCSMO (8%). The result is encouraging for the performance of CMR devices.

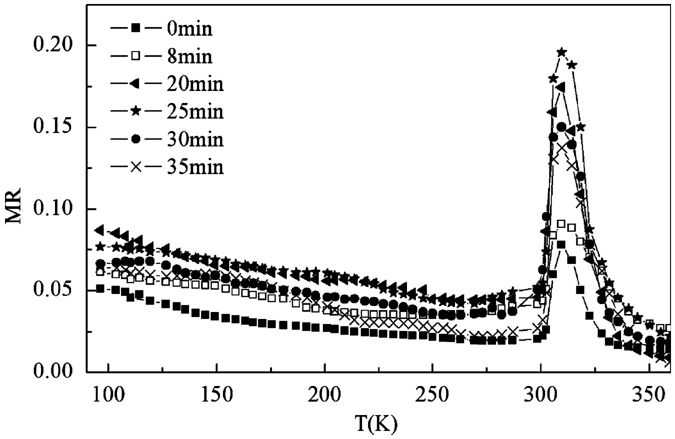

Fig. 5. The temperature dependence of magnetoresistive ratio for 1000 °C sintered composites LCSMO/*x*Ag with $x = 0$, 8, 20, 25, 30, and 35 min in the warming process. The applied field is 3000 Oe.

The enhancement of room temperature MR in the present system lies in two factors. Primarily, all samples have T_p (312 K), which is near room temperature. As has reported [14], the intrinsic CMR in perovskite compounds usually reaches its maximum near T_p. Secondly, the enhancement is attributed to the effect of Ag addition on the intrinsic MR of perovskite compounds. As discussed before, Ag improves the atomic disordered structure and magnetic inhomogeneity on the grain boundaries, which enhances the intrinsic properties of the composites and the decrease of ρ. And the ρ decrease is usually accompanied with an increase of MR. According to our results, we can know that $x = 25$ sample has an optimum improvement on the magnetic inhomogeneity and crystal structure of the LCSMO grains and grain boundaries. That results in the maximum MR values. However, for the composites with higher concentration of Ag, the grain boundaries become too thick and the LCSMO grains have less influence on ρ. As a result, the resistivity decrease in a field becomes slow and the relative change of the resistivity

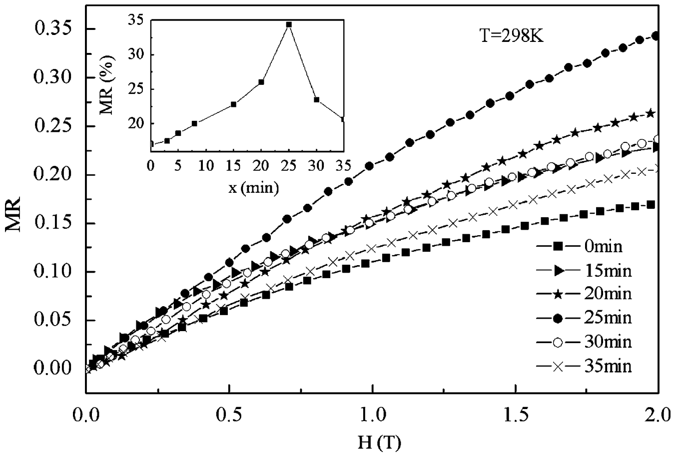

Fig. 6. Magnetic field dependence of the MR for the composites at 298 K. The inset is the different silver-plating time dependence of the variation of MR at 2 T.

becomes smaller and smaller. Hence, the MR decreases with high Ag content ($x>25$ min).

Fig. 6 shows the MR of some selected samples measured in a magnetic field range of 0–2 T at $T=298$ K. The inset is the MR versus plating time. An analysis of Fig. 6 shows that with increase in magnetic field from 0 to 2 T, the value of MR increases for all samples. In a given field, when $x=25$ min, the MR is as large as 35% and then decreases, which is in accordance with the results of the MR–T curve. As we have known that there are two influences of applied field on MR. One has to do with FM domain wall movement and the other has to do with grain boundaries of LCSMO [10]. In these LCSMO–Ag composites, Ag segregated at the grain boundaries plays a key role. For lower Ag addition ($x\leqslant 25$ min), the grain boundaries are thin and the applied magnetic field can easily align the domain walls along the field direction. So the MR increases until a maximum (35%) when $x=25$ min. However, for higher Ag addition, the grain boundaries become too thick and it is difficult for the applied field to align the domain walls along the field direction, so the MR effect weakens.

4. Conclusions

The Ag-doped LCSMO composites have been fabricated through an electroless plating process. The XRD and SEM results show that metal Ag does not enter the LCSMO lattice without disturbing the stoichiometry of LCSMO phase within the grains but segregates at the grain boundaries or surfaces. With increase of Ag content, T_P and T_C remain almost unchanged and σ_S decreases due to the dilution effect of nonmagnetic Ag, but values of MR are greatly enhanced for all samples. The maximum MR is as large as 19% near T_P under a low applied field (3000 Oe), almost 2.5 times larger than that of pure LCSMO (8%). At room temperature, a large MR value of 35% was observed at magnetic field of 2 T when $x=25$ min. All these results are encouraging for the performance of practical applications. We can suggest that the effect of Ag-added on the improvement of the grain boundaries is responsible for the enhancement.

Acknowledgments

This work was supported by the National Science Foundation of China (Grant no.10274022). The authors thank Analytical and Testing Center of Huazhong University of Science and Technology, which supplied us the facilities to fulfill the measurements.

References

[1] R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, K. Samwer, Phys. Rev. Lett. 71 (1993) 2331–2333.
[2] H.Y. Hwang, S.-W. Cheong, P.G. Radaelli, M. Marezio, B. Batlogg, Phys. Rev. Lett. 75 (1995) 914–917.
[3] P. Schiffer, A.P. Ramirez, W. Bao, S.-W. Cheong, Phys. Rev. Lett. 75 (1995) 3336–3339.
[4] X.L. Wang, S.X. Dou, H.K. Liu, M. Ionescu, B. Zeimetz, Appl. Phys. Lett. 73 (1998) 396–398.
[5] C. Zener, Phys. Rev. 82 (1951) 440.
[6] A.J. Millis, P.B. Littlewood, B.I. Shraiman, Phys. Rev. Lett. 74 (1995) 5144–5147.
[7] M. McCormack, S. Jin, T.H. Tiefel, R.M. Fleming, Julia M. Phillips, R. Ramesh, Appl. Phys. Lett. 74 (1994) 3045–3047.
[8] L.l. Balcells, A.E. Carrillo, B. Martínez, J. Fontcuberta, Appl. Phys. Lett. 74 (1999) 4014–4016.
[9] Chun-Hua Yan, Zhi-Gang Xu, Tao Zhu, Zhe-Ming Wang, Fu-Xiang Cheng, Yun-Hui Huang, Chun-Sheng Liao, J. Appl. Phys. 85 (2000) 5588–5590.
[10] Z.C. Xia, S.L. Yuan, W. Feng, L.J. Zhang, G.H. Zhang, J. Tang, L. Liu, S. Liu, G. Peng, D.W. Niu, L. Chen, Q.H. Zheng, Z.H. Fang, C.Q. Tang, Solid State Commun. 128 (2003) 291–294.
[11] Bao-xin Huang, Yi-hua Liu, Ru-zhen Zhang, Xiao-bo Yuan, Cheng-jian Wang, Liang-mo Mei, J. Phys. D: Appl. Phys. 36 (2003) 1923–1927.
[12] T. Tang, Q.Q. Cao, K.M. Gu, H.Y. Xu, S.Y. Zhang, Y.W. Du, Appl. Phys. Lett. 77 (2000) 723–725.
[13] Yun-Hui Huang, Ke-Feng Huang, Feng Luo, Lian-Long He, Zhe-Ming Wang, Chun-Sheng Liao, Chun-Hua Yan, J. Solid State Chem. 174 (2003) 257–263.
[14] J. Wu, S.Y. Zhang, Chin. Phys. Lett. 21 (2004) 382–385.
[15] Xiao-Bo Yuan, Yi-Hua Liu, Cheng-Jian Wang, Liang-Mo Mei, J. Phys. D: Appl. Phys. 38 (2005) 3360–3365.
[16] L.E. Hueso, J. Rivas, F. Rivadulla, M.A. López-Quintela, J. Appl. Phys. 86 (1999) 3881–3884.