Journal of Alloys and Compounds 480 (2009) 575–579

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Production of MgB_2 superconducting coatings by electrophoresis on metal substrates

R. Argyropoulou*, M. Ochsenkühn-Petropoulou

Laboratory of Inorganic and Analytical Chemistry, Department of Chemical Engineering, National Technical University of Athens, Iroon Polytechniou 9, 15773 Athens, Greece

ARTICLE INFO

Article history:
Received 3 August 2008
Received in revised form 27 January 2009
Accepted 30 January 2009
Available online 7 February 2009

Keywords:
MgB_2
Thick films
Electrophoresis
Sintering
SQUID

ABSTRACT

Production of MgB_2 coatings on various metallic substrates was achieved by means of the direct electrophoretic deposition technique. An inexpensive simple heat treatment in evacuated quartz tubes was developed as an alternative to inert gas flow during the process. The films were characterized by XRD, SEM and SQUID. It resulted that the procedure led to the production of uniform, dense and well-adhesive superconducting films. Stainless steel proved to be the best substrate among the investigated metals.

1. Introduction

The discovery of 39 K superconductivity in MgB_2 [1] has stimulated extensive research on the production of the material in several forms such as tapes [2], wires [3,4], thin and thick films [5–7]. The production of MgB_2 films and wires exhibits difficulties arising from the considerable volatility of magnesium and its high reactivity with oxygen. However, a number of techniques, such as pulsed laser deposition [8,9], sputtering [10], electrochemical process [11] and screen printing [6] have been employed for the production of MgB_2 films on various substrates. The electrophoretic deposition technique has not been widely used for the fabrication of MgB_2 thick films although it is an easy, fast and non-expensive method. There are a few reports on the electrophoretic production of MgB_2 films in two steps [12–14], consisting of the production of a boron film by electrophoresis followed by its heat treatment with magnesium. Nevertheless, Bodoardo et al. [15] have produced films in one step by electrophoretically depositing MgB_2 powder on Al_2O_3 substrates and heating the produced coatings at 850 °C for 90 min in Ar atmosphere. Ochsenkühn-Petropoulou et al. [16] have also produced MgB_2 films by electrophoresis in one step with a following heat treatment at 750 °C for 30 min under Ar flow. During this procedure, the main problem is the difficulty in achieving high air-tightness in the tube furnace and the prevention of MgO formation [17,18].

In this work, MgB_2 coatings were produced by direct electrophoretic deposition on various metallic substrates. For this purpose, a range of metals including Ag, Ni, Fe and stainless steel was investigated for their suitability. Moreover, an alternative method for the heat treatment of MgB_2 films on metal substrates produced by electrophoresis is presented. The products were characterized for their purity, homogeneity and superconducting properties by X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and magnetic susceptibility (SQUID).

2. Experimental

MgB_2 powder (Alfa – Aesar, 98% purity) was directly deposited by electrophoresis on commercial metal substrates (Ag, Ni, Fe and Stainless Steel). The chosen conditions of the electrophoretic deposition are the result of optimization in [19]. The as-prepared coatings together with segments of metal Mg were sealed in evacuated quartz tubes. The heat treatment was carried out in a tube furnace (Thermawatt, max. temp. 1100 °C), equipped with an automatic temperature controller. The samples were placed in the furnace directly at the working temperature and after the treatment were left to free cooling. The coatings were characterized by XRD (Siemens Diffractometer D5000), using Cu $K\alpha_1$ radiation, graphite monochromator, in a 2θ range 5–100°, counting time 1.0 s. The power conditions were 20 kV/30 mA. The patterns were evaluated by the DIFFRAC AT Search program. The microstructure of the samples was measured with SEM (Quanta 200, FEI Company) coupled with EDX (Genesis 4000). The superconducting properties were measured by dc-magnetization with a Quantum Design Magnetic Property Measurement System (MPMS, model 1822) equipped with a SQUID amplifier and a helium cryogenic system at the temperature range 5–50 K under 100 Oe applied magnetic field.

* Corresponding author. Tel.: +30 210 7724022; fax: +30 210 7724039.
E-mail addresses: rachel@ath.forthnet.gr, rachelargyropoulou@yahoo.gr (R. Argyropoulou).

0925-8388/$ – see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.jallcom.2009.01.121

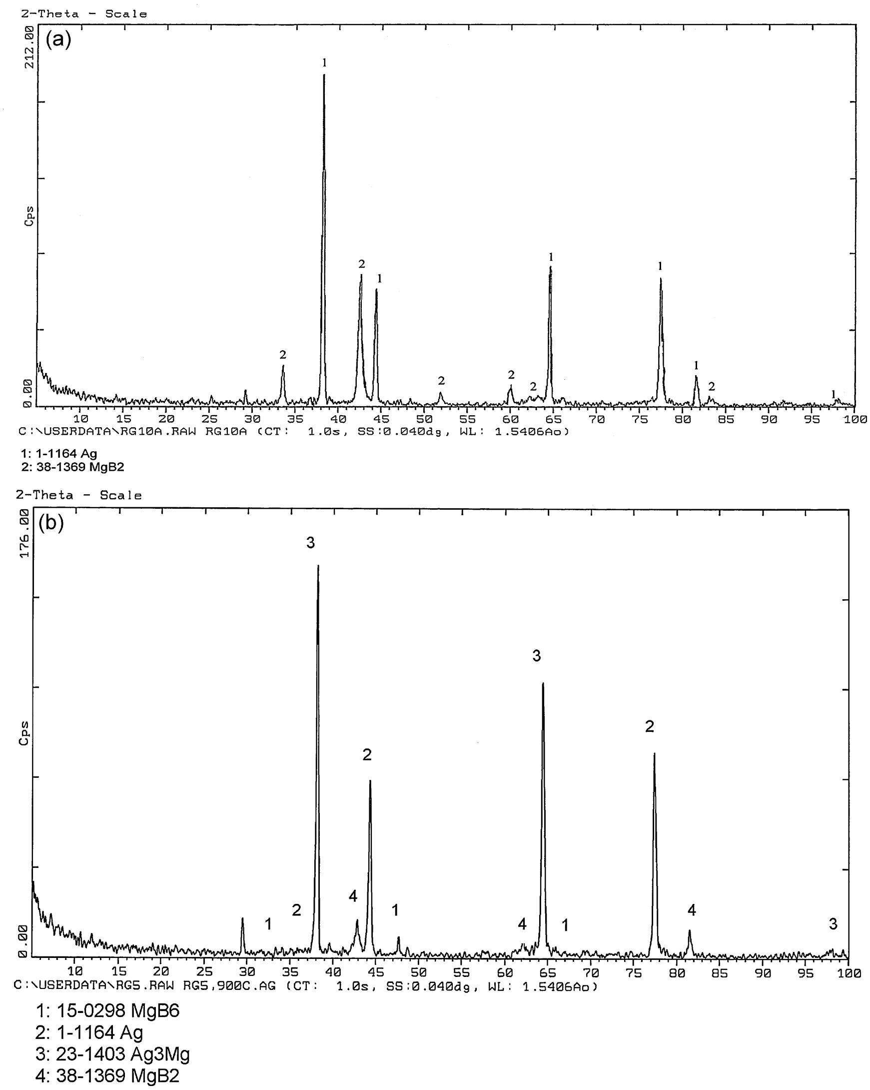

Fig. 1. (a) XRD spectrum of MgB_2 on Ag substrate heated at 750 °C for 20 min (1: Ag, 2: MgB_2). (b) XRD spectrum of MgB_2 on Ag substrate heated at 850 °C for 20 min (1: MgB_6, 2: Ag, 3: Ag_3Mg, 4: MgB_2).

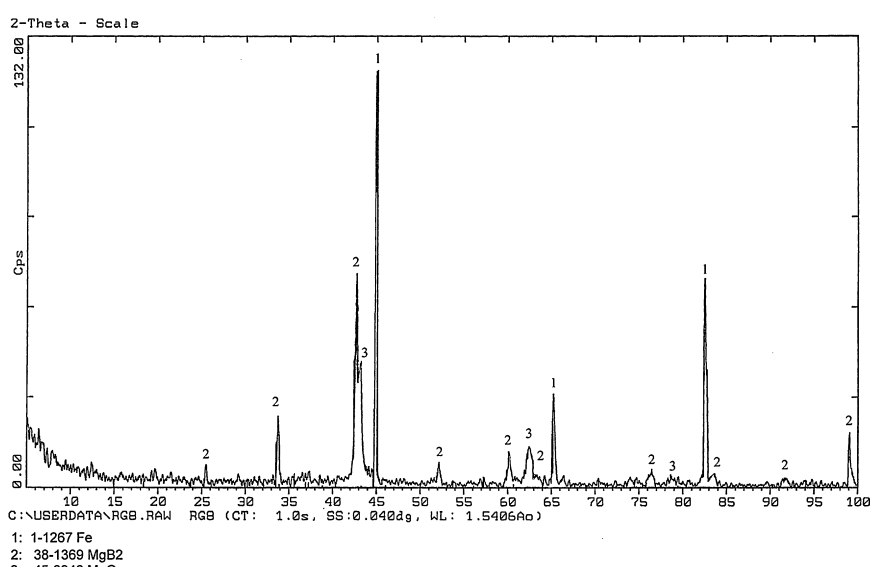

Fig. 2. XRD spectrum of MgB_2 on Fe substrate heated at 750 °C for 10 min (1: Fe, 2: MgB_2, 3: MgO).

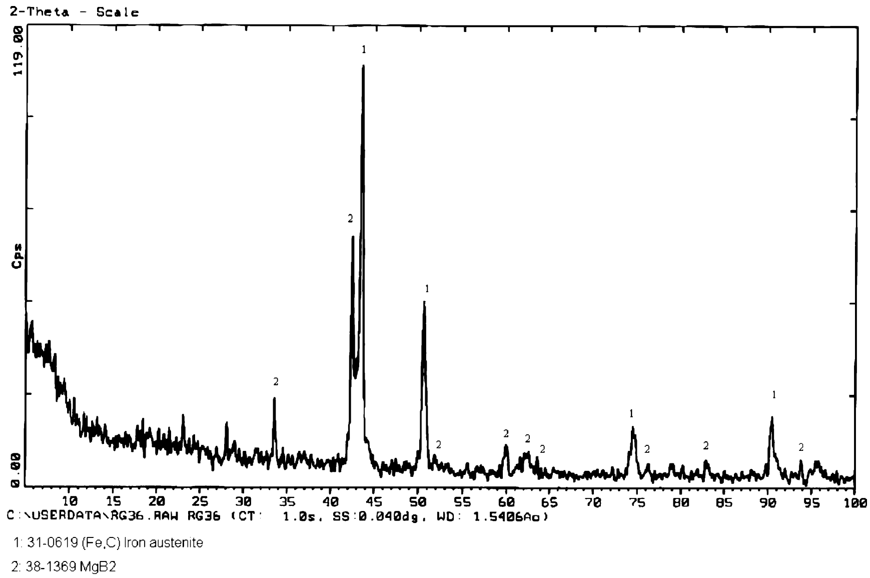

Fig. 3. XRD spectrum of MgB_2 on stainless steel substrate heated at 780 °C for 20 min (1: stainless steel, 2: MgB_2).

3. Results and discussion

It has been reported that during the production of MgB_2 films on metal substrates attention should be paid on the choice of the substrate as Mg and MgB_2 react with many metals forming solid solutions and intermetallics, degrading the superconductivity [20]. Moreover, it has been concluded [21–23] that the decomposition of MgB_2 is a matter of temperature and pressure: indeed the decomposition temperature of the material ~912 °C at 1 Torr decreases to 603 °C at 1 mTorr. Since the pressure in the quartz tubes of the present work was about 10^{-2} Torr, the sintering temperature of the samples should be much lower than 900 °C. On the other hand, low temperatures do not favor the adhesion between the substrate and the superconductor.

In an effort to overcome the above problems, the addition to the tubes of metal Mg segments was decided upon. Since the melting point of Mg is ~610 °C, at the temperatures investigated during this work the Mg could be partly evaporated in the tube, increasing in this way the pressure and preventing the decomposition of MgB_2. This addition would ensure an Mg excess and the ability to work at elevated temperatures as well.

In Fig. 1a the XRD spectrum of MgB_2 film on Ag substrate heated at 750 °C for 20 min is presented. As it is shown, at this temperature the decomposition of MgB_2 did not occur, as MgB_2 and Ag are the only phases present. However, by this treatment a poor adhesion between MgB_2 and Ag was achieved. By increasing the heating temperature at 850 °C and for the same heating period, the decomposition of MgB_2 took place resulting in the formation of MgB_6 and Ag_3Mg (Fig. 1b). The formation of MgB_6 was also observed at 800 °C. MgB_2/Ni films were also decomposed when heated at 850 °C. The decomposition was less than that with Ag substrates as MgB_6 formation in small ratio was observed in the XRD spectrum. On Ni substrate the MgB_2 did not decompose when heated at 750 °C for 15 min. The coating was high crystalline but MgB_2 did not attach well on the substrate and it could be easily removed. The observed poor adhesion between MgB_2 and Ni is in good agreement with the results of a previous work [7]. In the case of MgB_2/Fe coatings, the heat treatment at 850 °C for 20 min also resulted in a partial decomposition of the superconductor and the formation of MgB_6 phase in small concentration. MgB_2 on Fe substrate heated

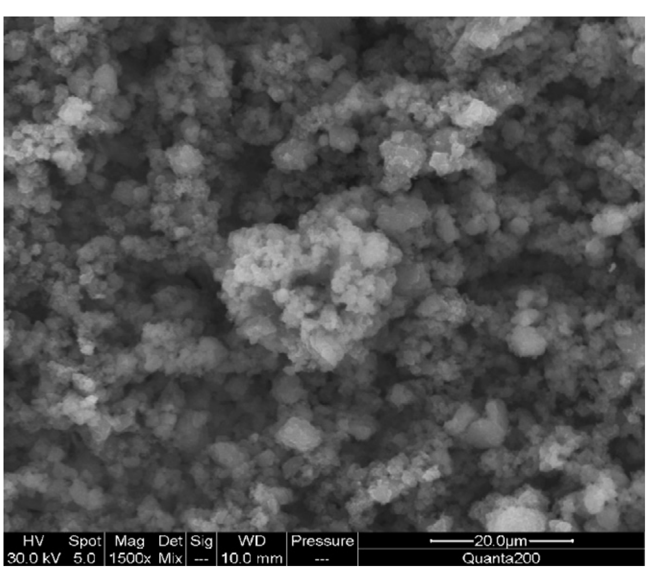

Fig. 4. SEM micrograph of MgB_2 on stainless steel substrate heated at 780 °C for 20 min.

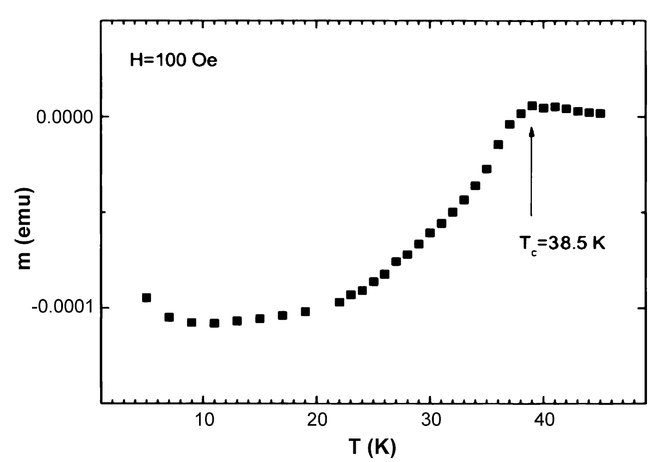

Fig. 5. Magnetization measurement vs. temperature at 100 Oe for MgB_2 on stainless steel substrate heated at 780 °C for 20 min.

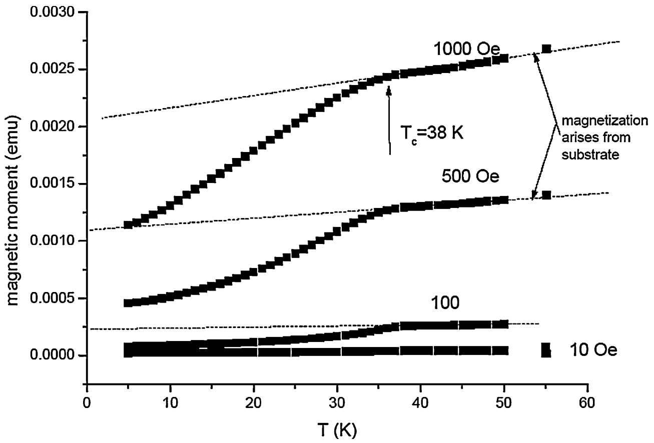

Fig. 6. Magnetization measurement vs. temperature at different applied magnetic fields for MgB_2 on stainless steel substrate heated at 780 °C for 20 min.

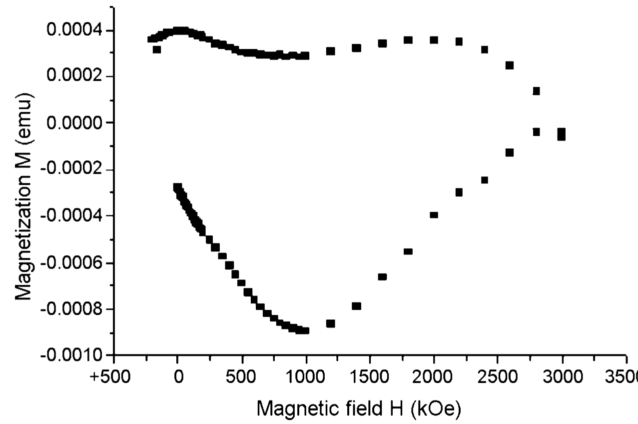

Fig. 7. Magnetic hysteresis loop of MgB_2/stainless steel coating at 5 K.

at 750 °C for 10 min gave encouraging results. The XRD spectrum of this sample is shown in Fig. 2. It is clear that no decomposition of MgB_2 occurred and the sample presented strong adhesion. The formation of MgO is attributed to the oxides of the substrate as Fe easily corrodes. The latter is a main disadvantage for the usage of Fe in film production as special protection should take place to prevent the formation of corrosion products which may decrease the compatibility of the metal with MgB_2 and the superconducting properties. Nevertheless, from the above results it is clear that the sintering process at elevated temperature (>800 °C) leads to the decomposition of MgB_2 with the parallel formation of undesirable impurities. Heating at lower temperatures (~750 °C) does not provoke the decomposition of MgB_2 but results in a loose attachment of the superconductor on the substrate with the exception of Fe. It should be mentioned that Majoros et al. [24] have also found out similar results. Based on these findings, stainless steel substrate was investigated in a range of heat treatment temperatures 730–800 °C and for a period of 10–30 min. In Fig. 3 the XRD spectrum of MgB_2 on stainless steel heated at 780 °C for 20 min is presented. No impurities or intermetallics were formed during the heat treatment. In the spectrum the only phases present belong to the superconductor and the substrate. Yao et al. [7] have also produced MgB_2 films on stainless steel substrates. They reported that their films were of poor adhesion, perhaps because of the difference on heat expanding coefficients between MgB_2 and the substrate. Nevertheless, the MgB_2/staineless steel films of this work did not exhibit any adhesion problem. This may be attributed to either a different chemical composition of the substrate compared to that of [7] or to the longer heating time.

The SEM observations of the produced film (Fig. 4) showed that the heating time of 20 min is enough for the sintering process since there are no voids between the grains. The average grain size was about 5 μm. The SQUID measurements of the film showed the, characteristic for the superconductor, critical onset temperature T_c of 39 K, with a ΔT_c of 10 K (Fig. 5). The wide slope of the curve can be attributed to an interference of the metallic substrate during the measurement.

The magnetization curves of the film at different applied magnetic fields are depicted in Fig. 6. As it can be seen, at very low field (10 Oe) the sign is low to be detected. At 100 Oe, the magnetic moment of the film is negative and the transition to the superconducting state occurs at 38 K. At higher magnetic fields, the paramagnetic sign of the substrate is added to the sign of the coating, resulting in a final positive magnetic moment. However, the film still presents a T_c of 38 K. These results confirm the interference of the substrate during the magnetization measurements. The magnetization loop of the film is presented in Fig. 7. For this measurement, the dimensions of the sample used were 0.2 cm × 0.2 cm and the thickness of the coating was 18 μm. From the Sun Model [25,26]

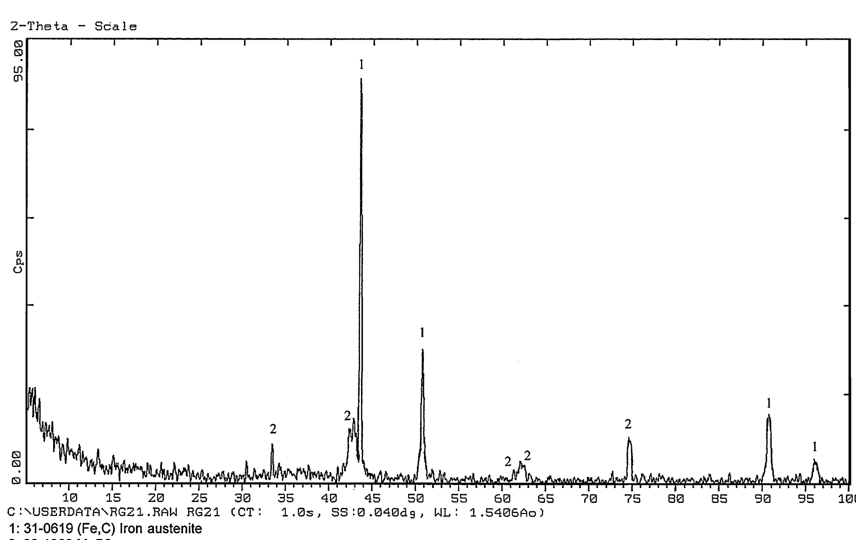

Fig. 8. XRD spectrum of MgB_2 on stainless steel treated without Mg segments (1: stainless steel, 2: MgB_2).

the critical current density J_c was calculated by the formula (1):

$$J_c(H) = 15 \cdot \frac{\Delta M(H)}{R} \quad (1)$$

where $\Delta M(H)$ (emu cm^{-3}) is the hysteresis width and R (cm) the radius of the surface of the coating. It resulted a value of $J_c = 2.18 \times 10^3$ A cm^{-2} at 5 K and 1200 kOe, which is in the range of other MgB_2 thick films [6,7].

In order to verify that the Mg segments in the tube contributed to the good quality of the film, an MgB_2 coating on stainless steel was sealed in an evacuated tube without the addition of metal. The results are presented in Fig. 8. This sample appears to be less crystalline than the previous one and the superconducting phase is present in a smaller ratio. The presence of unidentified small impurities can also be observed indicating that part of the superconductor decomposed during the heat treatment.

4. Conclusions

The developed electrophoretic deposition technique in one step can be applied for the production of MgB_2 superconducting coatings on metal substrates. The heat treatment of the samples can be achieved in evacuated tubes with the presence of Mg segments. The process is an alternative to inert gas flow in the furnace during the sintering procedure for the prevention of MgO formation and MgB_2 decomposition. By this procedure, dense coatings of high purity presenting the desired superconducting properties can be produced. Stainless steel is a promising metal substrate for MgB_2 films.

Acknowledgments

The authors acknowledge the Institute of Material Science of NCSR “Demokritos” and especially Dr. M. Pissas for the SQUID measurements.

References

[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu, Nature 410 (2001) 63–64.
[2] E. Bayazit, S. Altin, M.E. Yakinci, M.A. Aksan, Y. Balci, J. Alloys Compd. 457 (2008) 42–46.
[3] P. Kováč, W. Pachla, I. Hušek, M. Kulczyk, T. Melišek, T. Holúbek, R. Diduszko, M. Reissner, Phys. C 468 (2008) 2356–2360.
[4] L. Arda, S. Ataoglu, Z. Abdulaliyev, O.A. Sacli, J. Alloys Compd. (2008), doi:10.1016/j.allcom.2008.02.080.
[5] T.G. Lee, S.W. Park, W.K. Seong, J.Y. Huh, S.-G. Jung, B.K. Lee, K.-S. An, W.N. Kang, Phys. C 468 (2008) 1888–1891.
[6] R. Sakaguchi, Y. Ikebe, E. Ban, Y. Matsuoka, J. Alloys Compd. 452 (2008) 401–405.
[7] Q.W. Yao, X.L. Wang, S. Soltanian, A.H. Li, J. Horvat, S.X. Dou, Ceram. Int. 30 (2004) 1603–1606.
[8] Y. Zhao, M. Ionescu, A.V. Pan, S.X. Dou, E.W. Collings, Supercond. Sci. Technol. 16 (2003) 1487–1492.
[9] Y.S. Wu, Y. Zhao, D. Wexler, J.H. Kim, S.X. Dou, Phys. C 468 (2008) 218–222.
[10] A. O' Brien, B. Villegas, J.Y. Gu, Phys. C (2008), doi:10.1016/j.physc.2008. 10.006.
[11] H. Sakurai, T. Kuramochi, Y. Furuya, H. Oike, T. Kato, K. Hoshi, Phys. C 468 (2008) 1097–1099.
[12] Y.B. Zhu, J.D. Xu, S.F. Wang, Y.L. Zhou, Z.H. Chen, H.B. Lu, M. He, S.Y. Dai, Q. Zhang, G.Z. Yang, Phys. C 371 (2002) 7–9.
[13] S.F. Wang, Y.L. Zhou, Y.B. Zhu, Q. Zhang, Z. Liu, Z.H. Chen, H.B. Lu, S.Y. Dai, G.Z. Yang, Phys. C 390 (2003) 6–10.
[14] R.S. Hyam, K.M. Subhedar, S.H. Pawar, Colloids Surf. A: Physicochem. Eng. Aspects 315 (2008) 61–65.
[15] S. Bodoardo, C. Portesi, P. Fino, R. Gonnelli, M. Rajteri, E. Monticone, C. Badini, N. Penazzi, J. Eur. Ceram. Soc. 24 (2004) 1837–1840.
[16] M. Ochsenkühn-Petropoulou, L. Mendrinos, A. Altzumailis, R. Argyropoulou, J. Mater. Proc. Technol. 161 (2005) 16–21.
[17] M.B. Kadam, B.B. Sinha, R.S. Kalubarme, S.H. Pawar, J. Alloys Compd. (2008), doi:10.1016/j.allcom.2008.11.124.
[18] C. Terzioglu, A. Varilci, I. Belenli, J. Alloys Compd. (2008), doi:10.1016/j.allcom.2008.12.044.
[19] M. Ochsenkühn-Petropoulou, A. Altzumailis, R. Argyropoulou, K.M. Ochsenkühn, Anal. Bioanal. Chem. 379 (2004) 792–795.
[20] C. Buzea, T. Yamashita, Supercond. Sci. Technol. 14 (2001) 115–146.
[21] Z.K. Liu, D.G. Schlom, Q. Li, X.X. Xi, Appl. Phys. Lett. 78 (2001) 3678–3680.
[22] Z.Y. Fan, D.G. Hinks, N. Newman, J.M. Rowell, Appl. Phys. Lett. 79 (2001) 87–89.
[23] Q.Z. Shi, Y.C. Liu, Q. Zhao, Z.Q. Ma, J. Alloys Compd. 458 (2008) 553–557.
[24] M. Majoros, B.A. Glowacki, M.E. Vidkers, Supercond. Sci. Technol. 15 (2002) 269–275.
[25] J.Z. Sun, M.J. Scharen, L.C. Bourne, J.R. Schriesser, Phys. Rev. B44 (1991) 5275–5279.
[26] E. Moraitakis, M. Pissas, D. Niarchos, Phys. C 241 (1995) 63–70.