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Submicron-sized hybrid SiO_2–Ni powders produced with the sol-gel method

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Magnetic powders based on metallic nickel nanoparticles encapsulated in submicron-sized spherical silica shells have been obtained and investigated. The nickel clusters were produced by the exploding wire method. The silica shells were prepared via the modified sol-gel Stöber method, and the metallic particles were entrapped by their occlusion during silica powder formation. The obtained hybrid materials were investigated by electron microscopy, X-ray diffraction, magnetic, and ζ potential techniques. The obtained materials can potentially be employed in such applications as magnetically controlled drug vectors or electromagnetic field shielding.

Key words: *nickel particles; magnetic SiO_2–Ni particles; sol-gel method*

1. Introduction

Nanometer-sized metal and semiconductor particles have received much attention due to their novel properties, significantly different from those of the corresponding

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bulk materials, such as quantum-size effects, nonlinear optical properties and unusual magnetic properties [1–5]. Such particles are attractive dopants for a broad spectrum of matrices. One of the most promising host materials is submicron-sized powder obtained via the sol-gel technology. These have drawn considerable attention owing to their relative ease of preparation and various potential applications [6–10].

The sol-gel technique is based on the hydrolysis of liquid precursors and formation of colloidal sols [11–13]. The precursors are usually organosilicates (e.g., tetraethoxysilane, TEOS) which yield silicate sol-gel materials via the chemical reaction of hydrolysis

$$\equiv\mathrm{Si{-}OR} + \mathrm{H_2O} \longrightarrow \equiv\mathrm{Si{-}OH} + \mathrm{ROH} \tag{1}$$

and the subsequent formation of the silicate network:

$$\equiv\mathrm{Si{-}OH} + \mathrm{HO{-}Si}\equiv \longrightarrow \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{HOH} \tag{2}$$

$$\equiv\mathrm{Si{-}OR} + \mathrm{HO{-}Si}\equiv \longrightarrow \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{ROH} \tag{3}$$

As sol-gel materials are prepared from liquid solutions, the preparation process allows them to be doped by dissolving or suspending dopants in hydrolizates. An alternative way is to introduce various substances into sol-gel matrices via impregnation in solutions (suspensions) of the target molecules. A very attractive feature of the sol-gel technology is its application in manufacturing free and doped uniform silica spheres of submicron sizes [14–16].

The interesting and promising applications of sol-gel powders are based on SiO_2 submicron particles with dopants inducing a magnetic response. These materials could be used for vectorial drug administration and the control of their distribution, in magnetothermia or in magnetic resonance imaging [17–24]. These doped powders could also be applied as additives for textile coatings, various bulk plastics, or paints in order to induce their magnetic response (e.g., for electromagnetic radiation shielding). Since the size of the hybrid particles is less than 1 μm, however, the metallic magnetic particles need to be even smaller in order to achieve their encapsulation within the sol-gel silica shells.

The literature on sol-gel silica powders with magnetic inclusions is not very extensive and is usually limited to iron. Such materials have been usually made by the procedure developed for preparing conventional ferrofluids where mixtures of ferric and ferrous salts were appropriately reduced [20, 22, 25–30]. Attempts to entrap metallic particles are even less frequent. An example is the laser pyrolysis of ferrocene *in situ* during TEOS polymerization in a nebulized vapour cloud [17]. The entrapment of metallic nickel nanoparticles has been reported mainly for bulk silica materials obtained by the sol-gel method [31, 32].

The present work reports the sol-gel preparation of magnetic spherical submicron powders, in which the metallic nickel particles are entrapped within silica shells. The Ni particles were obtained by the exploding wire method [33–35]. The synthesized materials were investigated by various methods: electron microscopy, X-ray diffraction, magnetic, and ζ potential measurements. The obtained results indicate that the hybrid powders possess magnetic properties. These materials could be employed as additives introducing magnetic properties in various products, e.g. paints, plastics, and magnetically controlled drug vectors.

2. Experimental

The nickel nanopowders were obtained by exploding a 99.99% Ni wire (length 9 cm, ∅ 0.5 mm) in a 6 dm^3 vessel filled with 4 dm^3 of deionised water. The explosion was triggered by a current impulse of 50 kA for 23 μs at a condenser discharge voltage of 8.5 kV. During each synthesis, the procedure was repeated six times in order to accumulate more product. The powders were removed from water with magnetic field. A typical size of the obtained Ni particles was 20–40 nm.

The hybrid nickel-silica particles were prepared by the sol-gel method. 0.02 g of Ni nanopowder was ultrasonically dispersed in a mixture of 42×10^{-3} dm^3 of alcohol (methanol or ethanol), 7×10^{-3} dm^3 of distilled water, and 4×10^{-3} dm^3 of ammonia solution (25%, POCh). 3×10^{-3} dm^3 of tetraethoxysilane (Alfa Aesar) was added drop-wise to the dispersed mixture. Then, the suspension was agitated ultrasonically for 1 hour and the solvent was evaporated, yielding a grey powder.

One batch of the hybrid particles was dissolved in hydrofluoric acid (HF) in order to estimate their metal content. The metal clusters were held by a magnet and the supernatant was removed. The Ni particles separated in this way were washed with diluted NaOH solution and deionised water and dried.

The size and morphology of the hybrid powders were determined by scanning electron microscopy (XL 30 Philips CP) and transmission electron microscopy (TESLA BS 500). To investigate the crystal structure of the magnetic powders, a DRON-3 diffractometer (CoK_α radiation; λ = 0.178892 nm) was employed. The diffraction intensities were recorded within the 2θ range 20°–80° in steps of 0.05°. Magnetic properties of the materials were analysed by an in-house made Vibrating Sample Magnetometer (VSM). A Coulter Delsa 440 Doppler Electrophoretic Light Scattering Analyser was used for the ζ potential measurements in ultra-pure water.

3. Results and discussion

The sol-gel entrapment of nickel nanoparticles by SiO_2 shells was carried out in two different solvents (methyl and ethyl alcohols). As it can be seen from SEM (Fig. 1) and TEM (Fig. 2) micrographs, the methanol (MeOH) route yields smaller hybrid particles (MeNi) than the ethanol (EtOH) route (EtNi particles). It is important to note that in both cases the particles are almost perfectly spherical. Thus, the entrapment of the nickel particles in silica shells does not prevent the typical Stöber-like sol-gel process from yielding regular hybrid structures. Furthermore, a proper choice of the synthetic conditions (e.g. solvents) allows the product parameters (e.g., the grains size) to be controlled to a certain extent.

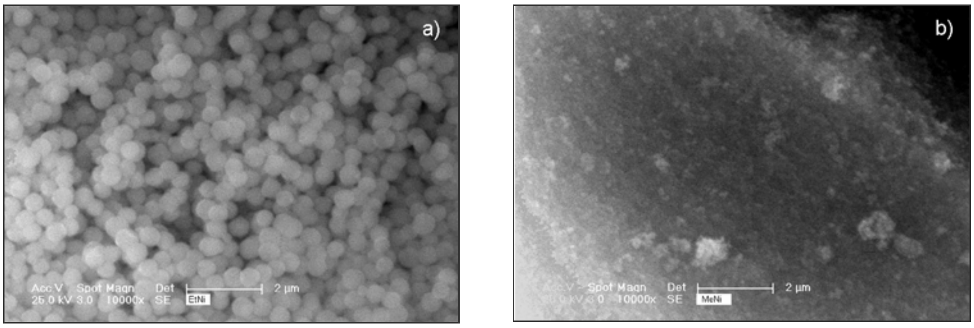

Fig. 1. SEM micrographs of EtNi hybrid particles (a) and MeNi particles (b)

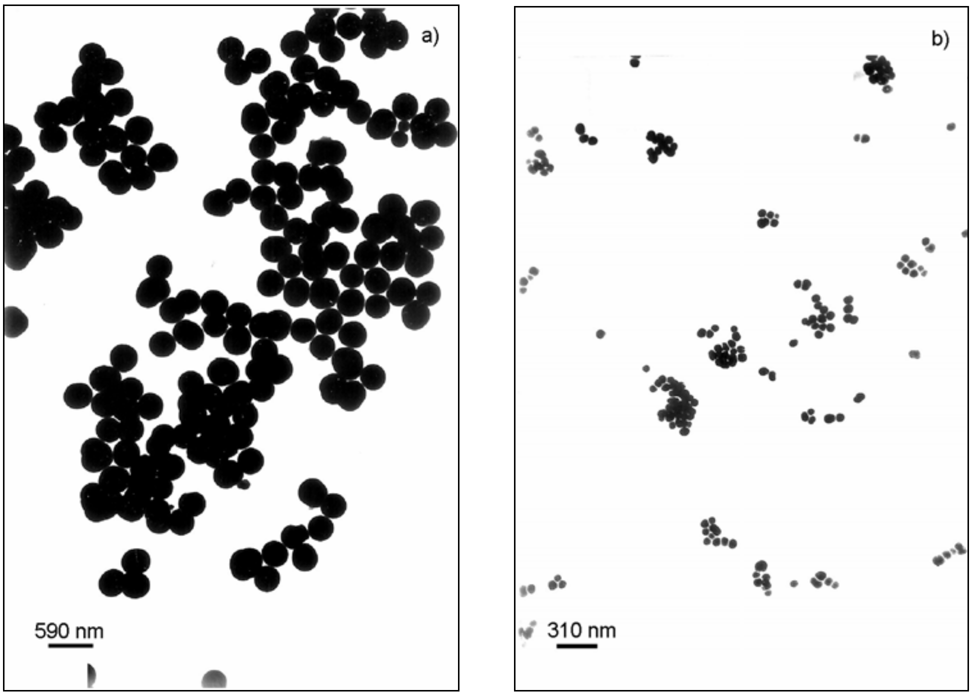

Fig. 2. TEM micrographs of EtNi hybrid particles (a) and MeNi particles (b)

Free metallic nickel particles and silica–metal hybrids were investigated by the XRD. The results are presented in Fig. 3. In addition to the metallic nickel (Ni) phase, a small amount of nickel oxide (NiO) is present. This presumably surface oxide can be the result of the fact that the nickel powders are obtained by wire explosion in water. In addition, the conditions during the sol-gel synthesis of the silica shells might also induce some surface oxidation of the metal particles.

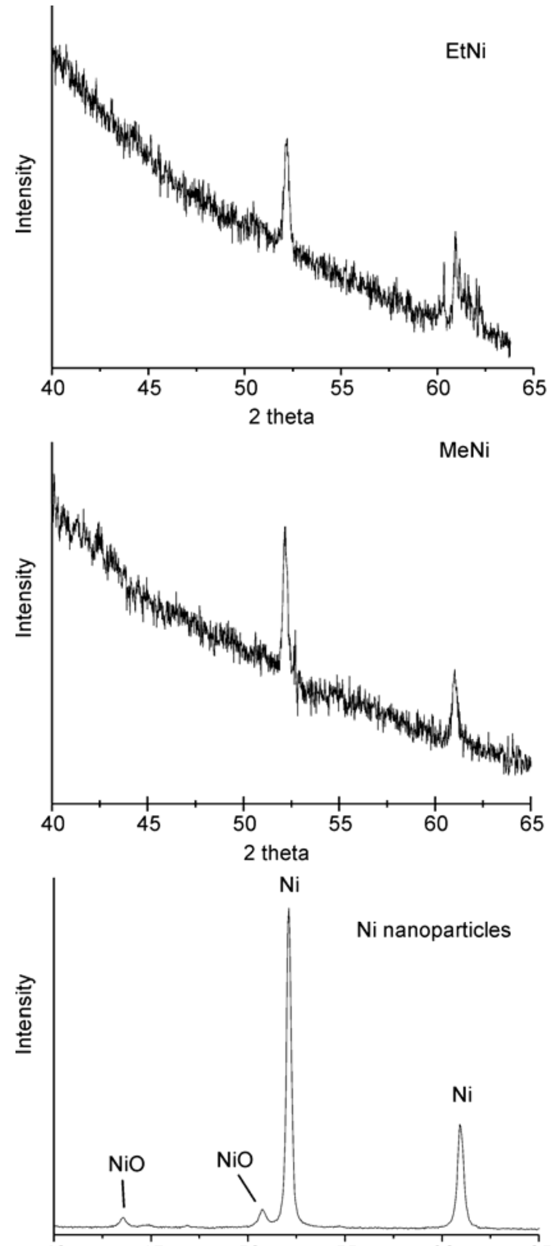

Fig. 3. The XRD patterns obtained for EtNi and MeNi hybrid SiO_2–nickel powders and for pure nickel nanoparticles

Figure 4 presents the distribution of the hybrid particle sizes obtained from the analysis of TEM results. The smaller particles (MeNi) have an average size of approximately 65 nm ($\varnothing \subset$ (50–80) nm), while the larger EtNi particles have an average diameter of ca. 350 nm ($\varnothing \subset$ (310– 390) nm). It is noteworthy that in both cases the fluctuations of grain size are relatively small, which is important from the point of view of potential applications.

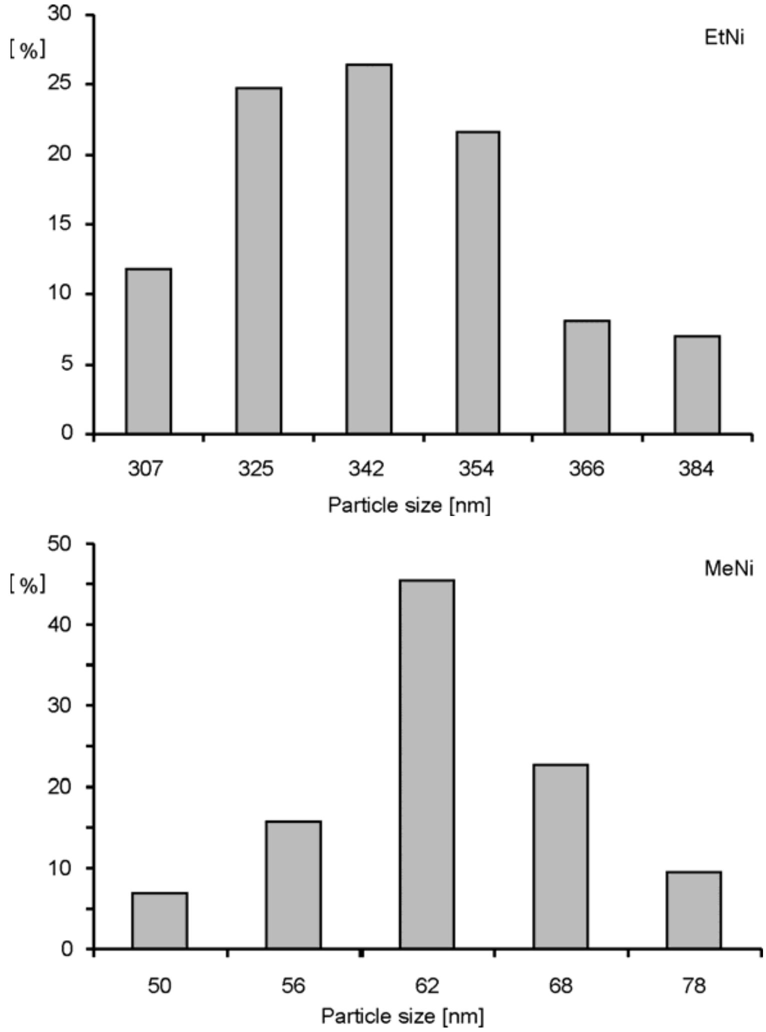

Fig. 4. Distributions of hybrid particles sizes

The ζ potential of pure (i.e. without any dopants) silica spherical particles produced via the ethanol route with the diameter of ca. 500 nm has been established to be –46.8 mV in pure water. This value is similar to results reported for other pure silica powders (–40.5 mV) [18] and for silica microspheres in water (–48 mV) [22]. The

ζ potential measured for the nickel-doped hybrid powders are –41.5 mV for the MeNi particles and –66.2 mV for EtNi. The EtNi hybrid particles may possess more terminal hydroxyl groups (which can be ionised in water) than the MeNi particles. This would mean larger negative surface charge and, consequently, higher absolute ζ potential.

The ζ potential observed for the pure silica particles, however, is lower than the one observed for the EtNi particles and comparable to the potential measured for the MeNi particles. This seems to indicate that the nickel–nickel oxide inclusions either increase the silica acidity (enhance surface hydroxyl group dissociation) or (and) increase the number of accessible surface –OH groups (e.g., due to the introduction of surface defects during silica spherical shell formation). Similar behaviour has been observed for iron nanoparticles entrapped in silica shells [36].

Figure 5 presents the magnetization curves obtained for silica-coated nickel particles at room temperature. From the shape of the curves, i.e. they approach magnetic saturation and exhibit hysteresis (not discernible in the figure), it appears that both powders are ferromagnetic. The hysteresis of the curves is relatively small: H_c = 8.5 mT for MeNi and H_c = 6.1 mT for EtNi. The hysteresis is slightly larger for particles with smaller size (MeNi). This increase in hysteresis could be related to the hysteretic behaviour of small particles approaching the single domain regime.

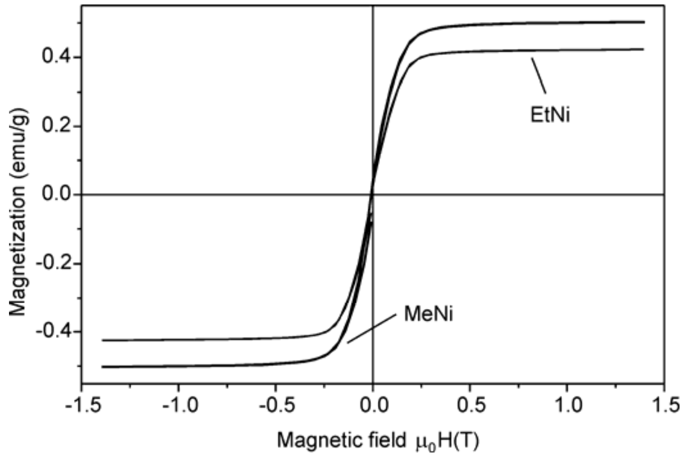

Fig. 5. Magnetization curves obtained for silica-coated nickel particles at room temperature

The saturation magnetization is slightly larger in the case of the smaller hybrid particles (MeNi; 0.51 emu/g) than for the larger particles (EtNi; 0.43 emu/g). This observation suggests that the efficiency of metallic particle entrapment was somewhat larger in the case of the smaller silica particles. Assuming that the dopant particles are pure nickel (the saturation magnetization of 54 emu/g at 20 °C), it is possible to estimate the weight percentage of nickel in the hybrid particles from the magnetic data.

This approach gives a nickel content of approximately 1.0% for the larger EtNi particles and 1.9% for the MeNi particles. These results are virtually identical to those for the magnetically separated nickel particles extracted from the silica shells with hydrofluoric acid. The magnetic measurement indicates that the amount of the residual nickel oxide is rather small, which corresponds well to the XRD data (Figure 3).

4. Conclusions

Ni nanopowders were successfully entrapped in spherical silica shells via the sol -gel method. The size of the hybrid particles depends on the alcohol solvent used during synthesis. Methanol yields smaller (ca. 65 nm; MeNi) and ethanol larger (ca. 350 nm; EtNi) Ni–SiO_2 particles. The X-ray diffraction data suggest that the free nickel particles contain very small amounts of the metal oxide (NiO), while clearly only the peaks corresponding to metallic nickel occur in the hybrid powder diffractograms. The pure silica spherical particles exhibit a ζ potential comparable to MeNi hybrid particles, while for EtNi it is higher. This suggests that Ni-dopant particles influence the surface chemistry of the hybrids. The Ni–SiO_2 particles display ferromagnetic behaviour at room temperature. The hybrid powder materials obtained could be used in magnetothermia, magnetic resonance imaging, as magnetically controlled drug vectors, or as additives for electromagnetic radiation shielding coatings.

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References

[1] GLEITER H., Acta Mater., 48 (2000), 1.
[2] BARD A.J., Science, 207 (1980), 139.
[3] BARD A.J., J. Phys. Chem., 86 (1982), 172.
[4] JOSELEVICH E., WILLNER I., J. Phys. Chem., 98 (1994), 7628.
[5] LESLIE-PELECKY D.L., RIEKE R.D., Chem. Mater., 8 (1996), 1770.
[6] PARK S.K., KIM K.D., KIM H.T., Colloids Surf. A: Physicochem. Eng. Asp., 197 (2002), 7.
[7] SADASIVAN S., RASMUSSEN D.H., CHEN F.P., KANNABIRAN R.K., Colloids Surf. A: Physicochem. Eng. Asp., 132 (1998), 45.
[8] RECULUSA S., MASSE P., RAVAINE S., J. Colloid Int. Sci., 279 (2004), 471.
[9] MONER-GIRONA M., ROIG A., MOLINS E., LLIBRE J., J. Sol-Gel Sci. Tech., 26 (2003), 645.
[10] ZUKOSKI C.F., Chem. Eng. Sci., 50 (1995), 4073.
[11] BRINKER C.J, SCHERER G.W., *Sol-Gel Science*, Academic Press, San Diego, 1990.
[12] KLEIN L.C., *Sol-Gel Optics*, Kluwer, Boston, 1994.
[13] REISFELD R., JORGENSEN C.K., *Chemistry, Spectroscopy and Applications of Sol-Gel Glasses,* Springer-Verlag, Berlin, 1992.

[14] WONG S., KITAEV V., OZIN G.A., J. Am. Chem. Soc., 125 (2003), 15589.

[15] BLANCO A., CHOMSKI E., GRABTCHAK S., IBISATE M., JOHN S., LEONARD S.W., LOPEZ C., MESEGUER F., MIGUEZ H., MONDIA J.P., OZIN G.A., TOADER O., VAN DRIEL H.M., Nature, 405 (2000), 437.

[16] JASIORSKI M., HRENIAK D., MARUSZEWSKI K., STRĘK W., Mater. Sci., 20 (2002), 51.

[17] BOMATÍ-MIGUEL O., LECONTE Y., MORALES M.P., HERLIN-BOIME N., VEINTEMILAS-VERDAGUER, J. Magn. Magn. Mater., 290–291 (2005), 272.

[18] CHAE K.P., LEE J.G., KWEON H.S., LEE Y.B., J. Magn. Magn. Mater., 283 (2004), 103.

[19] KORNAK R., MARUSZEWSKI K., STRĘK W., HAIMANN K., DUDZIŃSKI W., VOGT A.A., KOŁODZIEJ H.A., J. Alloys Comp., 380 (2004), 268.

[20] DORMER K., SEENEY C., LEWELLING K., LIAN G., GIBSON D., JOHNSON M., Biomaterials, 26 (2005), 2061.

[21] SUN Y., DUAN L., GUO Z., DUAN Y., MA M., XU L., ZHANG Y., GU N., J. Magn. Magn. Mater., 285 (2005), 65.

[22] ZHOU W., GAO P., SHAO L., CARUNTU D., YU M., CHEN J., O'CONNOR C., Nanomedicine: Nanotechnol., Biol., Medicine, 1 (2005), 233.

[23] MA Z.-Y., LIU X.-Q., GUAN Y.-P., LIU H.-Z., Colloids Surf. A: Physicochem. Eng. Asp., 275 (2006), 87.

[24] LEE J., ISOBE T., SENNA M., J. Colloid Int. Sci., 177 (1996), 490.

[25] ZHANG L., PAPAEFTHYMIOU G.C., ZIOLO R.F., YING J.Y., Nanostructured Mater., 9 (1997), 185.

[26] YASUMORI A., MATSUMOTO H., HAYASHI S., OKADA K., J. Sol-Gel Sci. Tech., 18 (2000), 249.

[27] ZHU Y., DA H., YANG X., HU Y., Colloids Surf. A: Physicochem. Eng. Asp., 231 (2003), 123.

[28] LIU X., MA Z., XING J., LIU H., J. Magn. Magn. Mater., 270 (2004), 1.

[29] ATARASHI T., KIM Y.S., FUJITA T., NAKATSUKA K., J. Magn. Magn. Mater., 201 (1999), 7.

[30] TARTAJ P., GONZALEZ-CARRENO T., BOMATÍ-MIGUEL O., SERNA C.J., BONVILLE P., Phys. Rev. B, 69 (2004), 94401.

[31] ISOBE T., WEEKS R.A., ZUHR R.A., Solid State Commun., 105 (1998), 469.

[32] ESTOURNES C., LUTZ T., HAPPICH J., QUARANTA T., WISSLER P., GUILLE J.L., J. Magn. Magn. Mater., 173 (1997), 83.

[33] KIM J.-S., Scripta Mater., 44 (2001), 2247.

[34] SABARI-GIRIA V., SARATHIA R., CHAKRAVARTHYB S.R., VENKATASESHAIAH C., Mater. Lett., 58 (2004), 1047.

[35] WANG Q., YANG H., SHI J., ZOU G., Mater. Sci. Eng. A, 307 (2001), 190.

[36] BORAK B., LASKOWSKI S., HECZKO O., AALTONEN A., BASZCZUK A., JASIORSKI M., SODENBERG O., MAZUREK B., OJA M., HANNULA S.-P., MARUSZEWSKI K., J. Sol.-Gel. Tech., 41 (2007), 185.

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