Microstructure and properties of superconducting, ferromagnetic and hybrid nanowire networks of La$_{1.85}$Sr$_{0.15}$CuO$_4$ and La$_{0.5}$Sr$_{0.5}$MnO$_3$

M. R. Koblischka$^{1,2}$, A. Koblischka-Veneva$^{1,2}$, X. L. Zeng$^1$, T. Karwoth$^1$

$^1$ Experimental Physics, Saarland University, P.O.Box 151150, 66041 Saarbrücken, Germany
$^2$ Superconducting Materials Laboratory, Department of Materials Science and Engineering, Shibaura Institute of Technology, Tokyo 135-8548, Japan
E-mail: miko@shibaura-it.ac.jp

Abstract. We have successfully fabricated La$_{1-x}$Sr$_x$MnO$_3$ (LSMO) nanowires with various $x$ level, and La$_{1.85}$Sr$_{0.15}$CuO$_4$ (LSCO) nanowires/nanoribbons via electrospinning. The colossal magnetoresistance (CMR) of the LSMO nanowire networks have been investigated, and the $T_c$ of the LSCO nanowires and nanoribbons are around 19.2 K and 29.3 K respectively. Furthermore, we have established a LSCO/LSMO nanowire hybrid system. From observation by scanning electron microscopy, the average diameter of the nanowires is around 220 nm and the average length can reach over 50 $\mu$m. The randomly aligned LSCO and LSMO nanowires show numerous connections and form a complicated hybrid network system. The nanowires are polycrystalline with the grain size of $\sim$30 nm as confirmed by transmission electron microscopy and EBSD. According to four-probe electrical transportation measurements, the superconductivity of the hybrid sample is suppressed and an anti-magnetoresistance effect is observed. SQUID measurements of $M(T)$ and $M(H)$ were carried out as well, revealing the soft magnetic character of the nanowires.

1. Introduction
Using the electrospinning technique [1, 2] it is possible to prepare ceramic superconducting and ferromagnetic nanowire networks from sol-gel type precursors [3–6]. In previous works, we could fabricate ferromagnetic La$_{1-x}$Sr$_x$MnO$_3$ (LSMO) nanowires with various doping levels $x$ [7] and superconducting La$_{1.85}$Sr$_{0.15}$CuO$_4$ (LSCO) nanowires [8]. LSCO was found to contain two different shapes of the nanoobjects: nanowires and nanoribbons. The latter ones are wide, but very thin nanowires which consist of practically one single layer of LSCO grains. Based on this experience it is natural to attempt the fabrication of a hybrid LSMO/LSCO nanowire network, and to study the resulting microstructures and physical properties like it was done in the literature for multilayered thin films or mixed powder samples of the two components. As the unit cells of the two materials are very similar to each other, the formation of multilayers does not introduce too much strain [9–14]. In the present contribution, we compare the microstructures of the two components and of the hybrid nanowire networks and discuss the resulting physical properties.
2. Experimental procedures

2.1. Electrospinning

![Schematic drawing of the electrospinning apparatus.](image)

Figure 1. Schematic drawing of the electrospinning apparatus. The blow-up shows the situation when using two orifices to produce hybrid materials from two different sources. The distance $d$ between the two orifices must be set properly to avoid interference effects.

Figure 1 presents a schematic drawing of the electrospinning instrument. The precursor is pushed by the microspeed boost pump from the syringe to the bottom of the needle. The precursor is dragged by the electric field between the needle and the grounding area, transforming the original droplets to nanofibers. This method is commonly used in the literature to prepare polymer nanofibers [1,2], and recently, also ceramic materials were demonstrated to be prepared using this technique [3–6]. The blow-up in Fig. 1 gives details about the use of two orifices for the spinning process of two component. Controlling the distance between two orifices as shown in the blue frame, it is possible to fabricate different materials simultaneously without interference with each other.

The electrospinning precursor is prepared by dissolving La, Sr, and Mn acetates in PVA (high molecular weight polyvinyl alcohol). The same process is carried out for LSCO using La, Sr, and Cu acetates. The PVA is slowly added to the acetate solution with a mass ratio of 2.5:1.5. This solution is stirred at 80°C for 2 h, and then spun into cohering nanofibers by electrospinning. To remove the organic compounds and to form the desired ceramic phases, the sample is subsequently heat treated in a lab furnace. The reaction temperature is chosen to be 700°C (1 h), which is close to the optimal temperature for LSCO. An additional oxygenation process is required to obtain the correct phase composition. Further details about the electrospinning process of these nanowires are given elsewhere [8, 15]. The constituent phases of the hybrid nanowire network samples were determined by means of a high-resolution automated RINT2200 X-ray powder diffractometer, using Cu-Kα radiation generated at 40 kV and a current of 40 mA.

2.2. Sample characterization

SEM/EDX imaging was carried out using a JEOL 7000 F SEM microscope operating at 15 kV. This microscope is further equipped with a TSL OIM analysis unt [16] for orientation imaging using the EBSD technique. More details about the EBSD measurements on such nanowire network samples can be found in [17]. TEM investigations were performed using a JEOL JSM-2011 transmission electron microscope operating at 200 KV with a LaB$_6$ cathode. For TEM and
3. Results and discussion

3.1. Microstructures
In our first experiments on LSCO nanowires, we found that two different types of nanoobjects result: nanowires and nanoribbons [8]. The nanoribbons are very thin, but wide, whereas the nanowires have a round cross section. Figure 2 presents SEM images of the LSCO nanowires and nanoribbons in the as-spun state directly after the electrospinning process (a,c) and after the heat treatment (b,d).

The as-spun polymer nanofibers are completely smooth and homogeneous. In contrast, the heat-treated nanowires and -ribbons show the resulting granular structure after the burn-off of the polymer and the ceramic grain growth. The images of the nanoribbons further show that the ribbons are so thin, being transparent to the electron beam. These structures were maintained during the whole thermal treatment. The average diameter of the nanowires was determined to about 234 nm. The flat nanoribbons showed widths which are \( \sim 1 \ \mu m \), but the corresponding...
Figure 3. LSCO TEM images. (a) and (b) show nanoribbons, which are transparent to the electron beam. Images (c) and (d) are bright field and dark field images to reveal the details of the LSCO grain arrangement.

thicknesses are only about 60 – 80 nm. The total lengths of these fibers were found to be above 50 µm; most of them were in the 100 µm range.

In Fig. 3, we present TEM images of the LSCO nanowires/nanoribbons. The resulting images reveal clearly that the samples are polycrystalline. The nanoribbons (a,b) consist of only one layer of grains, and show the presence of holes between the grains. The nanowires, shown here in bright and dark field images (c,d) to reveal the grain arrangement, exhibit the same shape of the grains as found at the nanoribbons, with well defined grain boundaries between the LSCO grains. The grain size statistics obtained from several TEM images shows a broad variation and the average grain size is determined to be about 110 nm. One should notice here that the grain size of the nanoribbons is equal to the thickness. This indicates that the nanoribbons are formed by individual LSCO grains, linked to each other in a single layer. For the LSMO samples, we only observed the presence of nanowires in all experiments carried out [7]. The resulting arrangement and shape of the LSMO grains is, however, very similar to the one of LSCO as expected from the similarity of the crystal structures.

Figure 4 presents a TEM image of the LSMO/LSCO hybrid sample (a). From such images, it is not possible to distinguish between the two components, therefore, we have applied EDX mapping to image the spatial distribution of the Mn and Cu ions [18]. As result, we find that the individual nanowires are either LSCO or LSMO, and no intermix has occured along the nanowires. This can be expected from the fact that first the precursor-containing polymer nanowires were formed by electrospinning, and the process to build-up the grains takes place only within a given wire. The situation may, however, be different in the interconnets between the wires, which are numerous in the resulting nanowire network. Such a situation is depicted in Fig. 3 (c,d). Figure 4 (b) presents the result of the X-ray analysis of the hybrid sample, and
Figure 4. TEM image (a) of several individual nanowires from a LSMO/LSCO hybrid sample, revealing the polycrystalline, randomly-oriented grain arrangement. EDX mapping on these nanowires demonstrated that LSCO and LSMO nanowires are well separated. (b) shows the result of the X-ray analysis, and (c) gives the grain size distribution of the hybrid sample.

(c) gives the grain size statistics. The Gauss fitting of the data yields an average grain size of 33.2 nm.

Figure 5 presents the result of an EBSD measurement of the grain orientation performed on a LSMO nanowire. For this purpose, we followed the approach described in Ref. [17], using the transmission-EBSD technique on a single nanowire piece, which is thin enough. In (a), the measured section of the LSMO nanowire is shown (green box); the image (b) gives the EBSD-orientation mapping in [001]-direction (perpendicular to the surface). The color code for the orientation mapping is given in the stereographic triangle. The mapping reveals the polycrystalline character, together with the numerous high-angle grain boundaries. The plots (c) and (d) give the distribution of the grain shape aspect ratio, and the EBSD-determined grain size distribution, which is even smaller (∼20 nm) as compared to the mean TEM value (33.2 nm). Thus, the EBSD analysis provides important additional information important for the evaluation of the MR data on such a sample.

3.2. Physical properties
In Fig. 6, we present the results of magnetization measurements on the nanowire networks. To obtain large enough magnetic signal, a certain amount of material is required for these measurements. In Fig. 6 (a), a $M(T)$ measurement on the LSCO nanowires/nanoribbons is presented, measured in field-cooling (FC) and zero field-cooling (ZFC) modes with an applied field of 1 mT. Here, we find two distinct superconducting transitions, $T_c$, at 29.3 K and at 13.9 K, respectively. We ascribe the two $T_c$ to the contributions of the nanowires and nanoribbons; the superconducting phase being better developed in the nanoribbons [8].

In Figs. 7 (a,b) the resistance versus temperature curves measured in various applied magnetic fields (0 T, 2.5 T, 5.0 T and 7.5 T, perpendicular to the sample surface) is presented in the temperature range $2 \text{ K} \leq T \leq 300 \text{ K}$ for the LSMO/LSCO hybrid sample (a) and the pure LSMO sample (b). The resistance of the LSMO/LSCO hybrid sample is obviously higher than that of the pure sample, showing the semiconducting behavior of LSCO in the normal regime. A comparison of the $R(T)$-data of the hybrid sample with the pure LSMO directly reveals an inversed field dependence.
Figure 5. EBSD analysis of a LSMO nanowire. (a) SEM image of the selected area and (b) orientation mapping in [001]-direction. The color code for the mapping is given in the stereographic triangle. The plot (c) gives distribution of the grain shape aspect ratio and (d) grain size distribution.

Figure 6. Magnetization measurements on the nanowire network samples. (a) gives an $M(T)$-measurement to demonstrate the onset of superconductivity in the LSCO nanowires. Two transitions can be seen – one at 29.3 K, the other at 13.9 K. (b) presents $M(H)$-loops at 300 K and at 10 K, showing weak ferromagnetic behavior.
Figure 7. Resistance-temperature $R(T)$ diagram and the MR ratio for the LSMO/LSCO hybrid sample (left) and the pure LSMO sample (right) as function of temperature.

Figures 7 (c,d) give the MR ratio for both types of samples. Magnetoresistance (MR) plots are calculated from the resistance data obtained by sweep measurements at different field strengths using the relation $MR[\%] = (R_H(T) - R_0(T))/R_0(T)$. From the MR plots of the LSMO/LSCO hybrid sample and the pure LSMO one, we can draw several interesting conclusions: (i) At low temperatures, the MR effect of the hybrid sample is clearly suppressed. (ii) The field dependence of the MR ratio is inversed, indicating a positive MR for the hybrid sample and a negative one for the pure LSMO sample as described previously in [7]. (iii) A large MR of $\sim 1120\%$ is obtained in the hybrid sample at a temperature of 280 K and 7.5 T applied field. This maximum MR is strongly decreasing with lowering the applied field. These remarkable results may have different origins, partly induced by the nanowire structure and the small grain sizes of the constituents. The grain size of both LSMO and LSCO, together with the small nanowire diameter of $\sim 220$ nm and the numerous interconnects between the individual nanowires in the nanowire network fabrics, provide a large number of interfaces, which the currents have to pass through. Both the grain boundaries and the interconnects between the wires lead to a scatter of the electrons, thus leading to a strong MR effect. The grain size effect on the MR properties was also previously discussed in [19, 20]. The grain size of the present nanowires is even slightly smaller as presented there. Thus, especially the high-field MR effect of the pure LSMO nanowires is clearly increased in our case. The role of superconductivity in the hybrid sample is also an important one. Even though our magnetic measurements could not reveal a superconducting diamagnetic contribution directly, the character of the interfaces between the nanowires is clearly changed. The superconducting signal may only be well developed within the LSCO grains, and there are not many interconnects between the wires as in these places an exchange between the two components becomes possible, and Mn ions may replace the Cu ions, leading to non-superconducting interconnects. The nature of these interconnects, therefore, determines the MR properties.
4. Conclusions
We have presented the fabrication and characterization of LSCO, LSMO and LSMO/LSCO nanowire hybrid network samples by electrospinning. The pure components are superconducting or ferromagnetic, but the hybrid sample exhibits interesting properties due to the combination of superconductivity and ferromagnetism and the resulting character of the interconnects between the individual nanowires.

Acknowledgments
We thank J. Schmauch (Saarland University, group Prof. Birringer) for technical assistance and Prof. V. Presser for the use of the electrospinning apparatus. This work is supported by DFG grant Ko2323/8, which is gratefully acknowledged.

References
[1] Z. M. Huang, Y. Z. Zhang, M. Kotaki, S. Ramakrishna, "A review on polymer nanofibers by electrospinning and their applications", Composites Science Technol. 63, 2223 (2003).
[2] D. Li, Y. N. Xia, "Electrospinning of nanofibers: Reinventing the wheel?". Adv. Mater. 16, 1151(2004).
[3] Li D, McCann J T and Xia Y N 2006 Electrospinning: A simple and versatile technique for producing ceramic nanofibers and nanotubes. J Am Ceram Soc 89 1861
[4] Wu H, Pan W, Lin D and Li H 2012 Electrospinning of ceramic nanofibers: Fabrication, assembly and applications. J Adv Ceramics 1 2
[5] Li D, Herricks T and Xia Y N 2003 Magnetic nanofibers of nickel ferrite prepared by electrospinning. Appl Phys Lett 83 4586
[6] Yensano R, Pinitsoontorn S, Amornkitbamrung V and Maensiri S 2014 Fabrication and magnetic properties of electrospun La$_{0.7}$Sr$_{0.3}$MnO$_3$ nanostructures. J Supercond Novel Mag 27 1553
[7] Karwoth T, Zeng X L, Koblishchka M R, Hartmann U, Chang C, Hauet T and Li J M 2019 Magnetoresistance and structural characterization of electrospun La$_{1-x}$Sr$_x$MnO$_3$ nanowire networks. Solid State Commun 290 37
[8] Zeng X L, Koblishchka M R and Hartmann U 2015 Synthesis and characterization of electrospun superconducting (La,Sr)CuO$_2$ nanowires and nanoribbons. Mat. Res. Express 2 095022
[9] Liu J M, Huang Q, Li J, Ong C K and Lin Z G 1999 Pulsed laser deposition of perovskite La$_{0.7}$Sr$_{0.3}$MnO$_3$/La$_{0.7}$Sr$_{0.3}$CoO$_3$ multilayers and their magnetotransport properties. Appl Phys A 69(suppl.) S663
[10] Li B, Chopdekar R V, N’Dinaye A T, Mehta A, Paige Byers J, Browning N D, Arenholz E and Takamura Y 2016 Tuning interfacial exchange interactions via electronic reconstruction in transition-metal oxide heterostructures. Appl Phys Lett 109 152401
[11] Yan C H, Xu Z G, Zhu T, Wang Z M, Cheng F X, Huang Y H and Liao C S 2000 A large low field colossal magnetoresistance in the La$_{0.7}$Sr$_{0.3}$MnO$_3$ and CoFe$_2$O$_4$ combined system. J Appl Phys 87 5588
[12] Li X H, Huang Y H , Wang Z M and Yan C H 2002Tuning between negative and positive magnetoresistance in (La$_{0.7}$Sr$_{0.3}$MnO$_3$)$_{1-x}$(La$_{1-x}$Sr$_{1.98}$MnO$_4$)$_x$ composites. Appl Phys Lett 81 307
[13] Habermeier H U, Cristiani G, Kremer R K, Lebedev O and van Tendeloo G 2001 Cuprate/manganese superlattices: A model system for a bulk ferromagnetic superconductor. Physica C 364-365 298
[14] Yao X, Jin Y, Li M, Li Zh, Cao G, Cao Sh and Zhang J 2011 Coexistence of superconductivity and ferromagnetism in La$_{1.85}$Sr$_{0.15}$CuO$_2$-La$_{2}$Sr$_{1.8}$MnO$_3$ matrix composites. J Alloy Compounds 509 5472
[15] Zeng X L, Koblishchka M R, Karwoth T, Hauet T and Hartmann U 2017 Preparation of granular Bi-2212 nanowires by electrospinning. Supercond Sci Technol 30 035014
[16] TexSEM Laboratories (TSL). Orientation Imaging Microscopy Software V4.1, User Manual, TexSEM laboratories, (TSL), Draper, UT, 2004.
[17] Koblishchka-Veneva A, Koblishchka M R, Zeng X L, Schmauch J and Hartmann U 2018 TEM and electron backscatter diffraction analysis (EBSD) on superconducting nanowires. J Phys Conf Ser 1054 012005
[18] Zeng X L, Koblishchka M R, Karwoth T and Hartmann U 2019 Properties of La$_{1.85}$Sr$_{0.15}$CuO$_4$/La$_{0.7}$Sr$_{0.3}$MnO$_3$ hybride nanowire networks prepared by electrospinning. J Magn Magn Mater 475 741
[19] Kar S, Sarkar J, Ghosh B and Raychaudhuri A K 2007 Effect of grain boundaries on the local electronic transport in nanostructured films of colossal magnetoresistive manganites. J Nanosci Nanotech 7 2051
[20] Balcelds Ll, Fontcuberta J, Martinez B and Obradors X 1998 High field magnetoresistance at interfaces in manganese perovskites. Phys Rev B 58 R14697