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Physica B 320 (2002) 115–118

PHYSICA B

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Nonlinear behavior of V–I curves at low temperatures in nanoparticles of $La_{2/3}B_{1/3}MnO_3$ with B = Ca, Sr

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Abstract

We measure voltage–current curves at low temperature in $La_{2/3}B_{1/3}MnO_3$ samples (B = Ca, Sr). The powder oxides were prepared by different wet-chemical routes and low calcination temperatures were used for nanoparticles formation. We studied samples prepared by three different synthesis methods: gel-combustion, urea sol–gel and liquid-mix. Although the average particle size was almost the same for all the samples ($\sim$30 nm), we found different behaviors in the V–I curves depending on the synthesis route. The obtained data are analyzed in the electronic tunneling picture.

Keywords: Grain boundaries; Electrical resistivity; Tunneling

After the discovery of the "colossal magnetoresistance" (CMR) in manganites, an important low-field MR was observed in polycrystalline samples [1], films [2] and small particles [3], but not in single crystals. This behavior is related to the microstructure of the grain boundaries (gb) and is understood in terms of spin-polarized tunneling [1] at the gb. In general, at low temperatures ($T \leqslant 60$ K) an increase of resistivity (ρ) is found, which has been attributed to the Coulomb blockade in small particles [4]. In this T range, associated to the presence of a tunneling barrier a nonlinear response of ρ is expected. However, in the case of manganites the voltage–current (V–I) curves have not been explored enough.

In this work we study the electrical properties of $La_{2/3}B_{1/3}MnO_3$ samples (B = Ca, Sr), synthesized at low T by wet-chemical methods: urea sol–gel (USG), liquid-mix (LM) and gel-combustion (GC). In particular, we analyze the V–I characteristics of these samples.

We used three synthesis methods which start from nitrates of the desired cations, and a precursor gel is formed by adding organic compounds: urea for USG [5], citric acid and ethylene glycol for LM [6], and citric acid and ammonium hydroxide for GC [7]. While in the USG and LM routes this gel is slowly decomposed by heating at low T (250–450°C), in the GC process it burns due

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0921-4526/02/$ - see front matter
PII: S0921-4526(02)00657-9

to an intense exothermic redox reaction between nitrate and citrate ions. The powder is finally calcined at a synthesis temperature T_s of 600–800°C in order to form the perovskite. The phase formation was checked by means of X-ray diffraction. The particle size was determined by the X-ray line broadening method and by TEM observations. For the ρ measurements, the powders were pressed and fired at T_s for 10 min to weld the grains and form a pellet.

The resistivity of manganites is well known, and it has been established that ρ increases with decreasing particle size (D). As shown in Fig. 1, all our samples present a semiconducting behavior for T above T_{MI}, where a maximum of ρ is observed. Below this T the samples are metallic until T_{CB} is reached, where an insulating behavior is manifested again. The insulator-like tail of ρ at low T has been attributed to the Coulomb blockade. The blockade occurs when a charge carrier has to move from a neutral grain to a neighboring one, thus the charging energy makes difficult the carrier motion (see Fig. 1 at $T \leqslant 60$ K). Note that for the same D, the ρ of samples prepared by the different methods follow the order $\rho_{GC} > \rho_{USG} > \rho_{LM}$, implying that the strength of the gb barriers decrease in the same direction. Consistently, the more pronounced low-T tail occurs in the GC sample. The USG–La–Ca-II sample, with $D \approx 95$ nm has the minimum ρ, and a low-T increase of ρ is almost not observed.

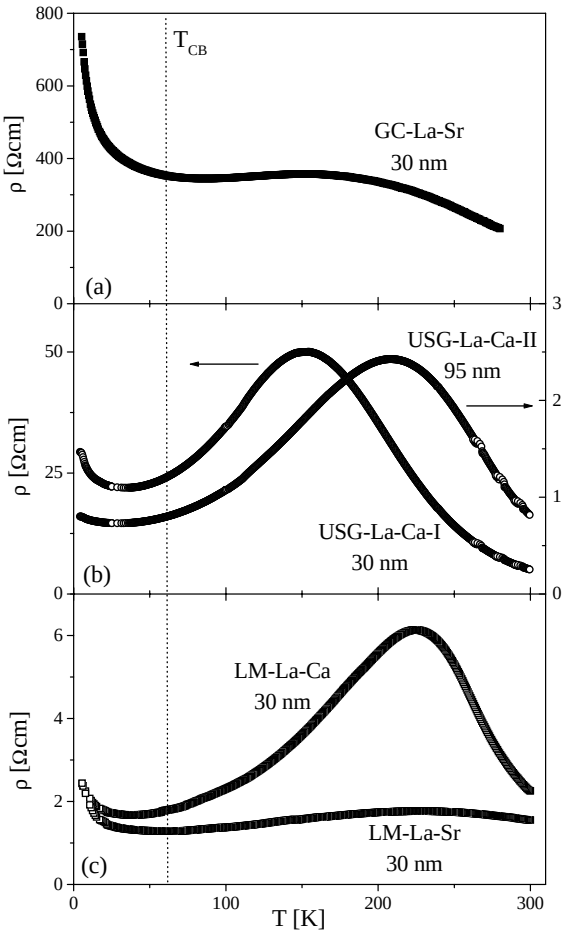

Fig. 1. ρ vs. T. (a) $La_{2/3}Sr_{1/3}MnO_3$ by GC, (b) $La_{2/3}Ca_{1/3}MnO_3$ by USG at 700°C (I-30 nm) and 800°C (II-95 nm). (c) $La_{2/3}Sr_{1/3}MnO_3$ and $La_{2/3}Ca_{1/3}MnO_3$ (30 nm) by LM method.

We now explore the V–I response of the different samples at low T, where the effect of the intergrain barrier is more important. The V–I curves were measured at several T with applied magnetic field (H) up to 9 T. In Fig. 2 we show the results at $T = 5$ K for $La_{2/3}Sr_{1/3}MnO_3$ nanoparticles prepared by GC. An important change of slope is observed, from R_0 at low V to R_{HV} at high V. The tunneling process dominates the charge transport at low V, while at high V the electric field overcomes the energy barrier. Therefore, we associate the high V response to the ohmic (linear)

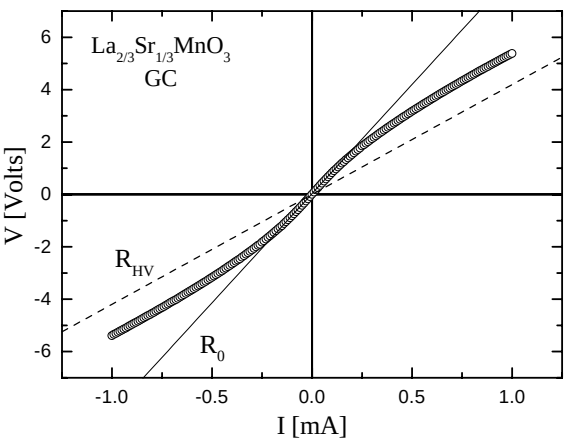

Fig. 2. Voltage vs. current at 5 K for $La_{2/3}Sr_{1/3}MnO_3$ prepared by GC. R_0 and R_{HV} are the resistances at zero and high voltage, respectively.

regime. To separate the tunneling contribution, we obtain the differential resistance dV/dI. Then, assuming a negligible contribution of the tunneling process at high V, the tunnel resistance R_{tun} can be obtained by subtracting the ohmic contribution, i.e., $R_{tun} = A((dV/dI) - R_{HV})$, where A is the cross area of the sample. Fig. 3 shows the resulting R_{tun} vs. V curves at several H. The nonlinear tunneling response is now well evidenced. By increasing both D and T the effect diminishes, being totally absent at $T > T_{CB}$. With the application of a magnetic field R_{tun} decreases. In the inset of Fig. 3 we show the $R_{tun}(V = 0)$ vs. H curve at 5 K, whose behavior is the well-known response of granular materials, usually associated to the spin-polarized tunneling of carriers across the gb barriers.

In the nanoparticles of $La_{2/3}Ca_{1/3}MnO_3$ prepared by USG, with $D \approx 30$ nm (USG–La–Ca-I in Fig. 1), the nonlinear behavior is also observed. However, some differences were found. The R_{tun} vs. V curves of this sample at 4.2 K and various H are shown in Fig. 4. It is clear that the nonlinear R_{tun} is also present, but a remarkable shoulder appears at $V \approx 0.5$ V and the peak-like shape of the curves at $V = 0$ differs from the smooth variation exhibited by the Sr-doped GC sample. Consequently with the lower ρ, the R_{tun} of the USG–La–Ca-I sample is 10 times lower than that of the GC one. We mention that the USG–La–Ca-I sample was prepared at $T_s = 700°C$. The USG–La–Ca-II sample ($D = 95$ nm) was prepared at 800°C [8], and contrary to the above results it exhibits well-linear V–I curves, thus R_{tun} is negligible in this sample.

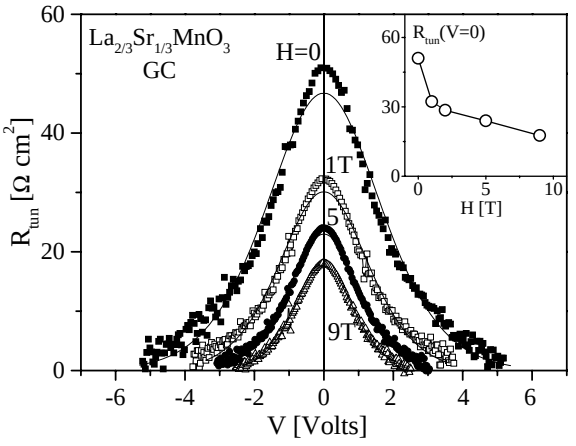

Fig. 3. R_{tun} vs. V for $La_{2/3}Sr_{1/3}MnO_3$ prepared by GC at various H. The lines are fits using a tunneling model [9]. Inset: $R_{tun}(V = 0)$ as a function of H.

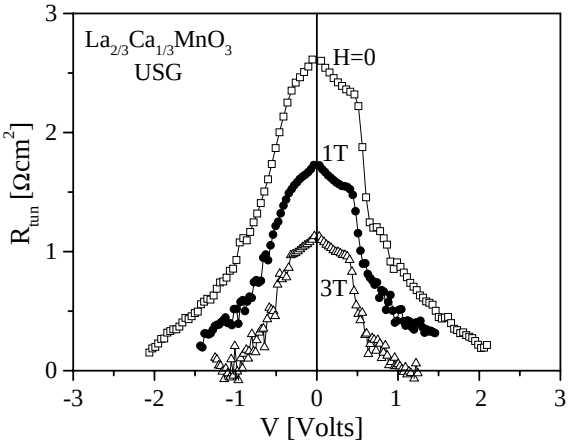

Fig. 4. R_{tun} vs. V for $La_{2/3}Ca_{1/3}MnO_3$ prepared by USG at different H.

Finally, in $La_{2/3}Sr_{1/3}MnO_3$ and $La_{2/3}Ca_{1/3}MnO_3$ prepared by LM at $T_s = 600°C$, the nonlinearity is almost absent, so both compounds show a very reduced R_{tun}. At $V = 0$ the Sr and Ca compounds present $R_{tun} \sim 0.04$ and $0.02\ \Omega\ cm^2$, respectively, much lower than those values shown in Figs. 3 and 4.

The key question is what causes the different samples to exhibit such a different intergrain barriers that produce notable changes in the ρ behavior. First of all we note that the strength of the barrier does not depend appreciably on the dopant (Sr or Ca). There are two possibilities: one is that the grain size determines the effective barrier through the Coulomb blockade. This explanation is compatible with the behavior of the USG samples, where for $D \approx 30$ nm an appreciable R_{tun} is measured while for $D \approx 95$ nm it is not observed. However, the extremely low R_{tun} in the LM samples which also have $D \approx 30$ nm contrasts with that idea. The second possibility is that the grain size plays a minor role, while the important effect is found in the microstructure of the gb. In this frame it should be expected that some organic residues at the gb generate the

insulating barrier. Therefore, the GC synthesis method would leave the highest amount of these residues, while the LM one would produce almost "clean" gb. The behavior of the USG–La–Ca-II sample would be consistent if we assume that at higher T_s (800°C instead of 700°C) the organic residues are totally eliminated. As a result, the GC would be the most appropriate to create gb insulating barriers leading to an important low-field MR.

In 1963, Simmons [9] derived a model for the electronic tunneling effect through a potential barrier. One of the parameters of the model, necessary to describe the R_{tun} vs. V curves is the height of the tunnel barrier (φ). A rough fitting of our experimental curves using this model (solid lines in Fig. 3) has given for the GC sample $\varphi_{GC} \approx 5.8$ V, for the USG–La–Ca-I sample $\varphi_{USG} \approx 2.2$ V and for the LM samples $\varphi_{LM} \approx 0.02$ V. These results agree with the idea that the GC method gives the highest gb insulating barrier.

In conclusion, we report how the synthesis method affect the V–I characteristics of $La_{2/3}B_{1/3}MnO_3$ at low T, where we clearly detect a nonlinear behavior generated by the gb insulating barriers. In this frame, the microstructure of the gb appears to be the relevant factor. By increasing the synthesis temperature the intergrain barrier is diminished, so the transport properties of the gb are changed. As a result, the resistivity is lowered and the nonlinearities disappear. Finally, we show that the GC method is appropriate to create insulating barriers between the grains that enhance the electronic tunneling effect.

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