Comparative study of the structural and magnetic properties of nanosized $La_{0.7}Ca_{0.3}MnO_3$ obtained by mechanochemical and glycine nitrate procedure

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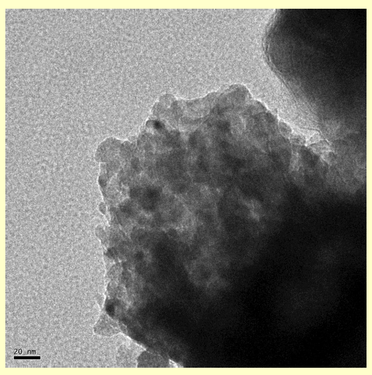
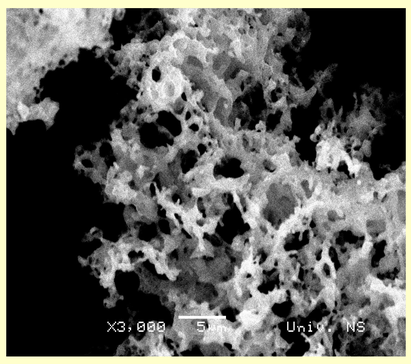
Mixed valent nanosized $La_{0.7}Ca_{0.3}MnO_3$ was prepared by two different synthesis routes: mechanochemical milling and glycine nitrate procedure. Microstructural characterization was performed by TEM microscopy and XRD measurements. These measurements showed that applied synthesis routes give samples with different morphologies, particle's sizes and distributions, as well as lattice parameters and microstrains. As a consequence of these specific microstructural features, different magnetic properties, like blocking temperatures, saturation magnetizations and coercive fields are observed. Evolution of microstructural and magnetic characteristics with sample annealing are discussed.

La0.7Ca0.3 MnO3

glycine nitrate procedure

La(NO3)3 6 H2O, Ca(NO3)2 6 H2O, Mn(NO3)2 4 H2O and glycine (C2H5NO2) were dissolved in distiller water to form the precursor solution. After heating at 200 C and dehydratation and self combustion reaction nanosized sample was obtained.

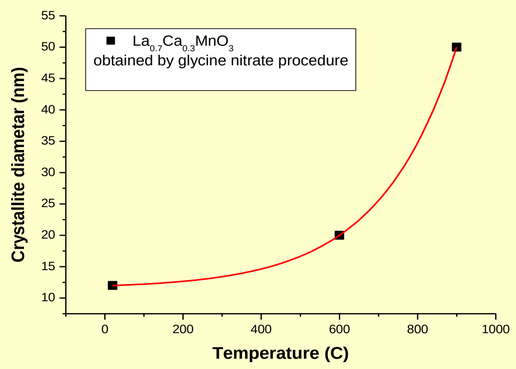


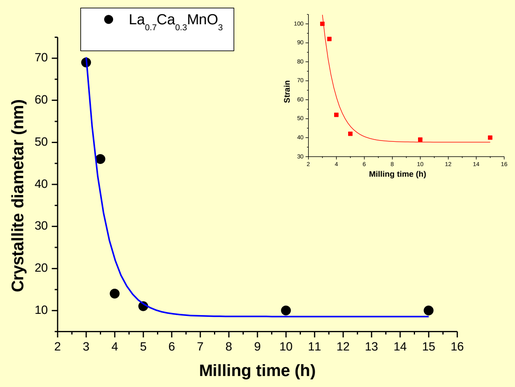


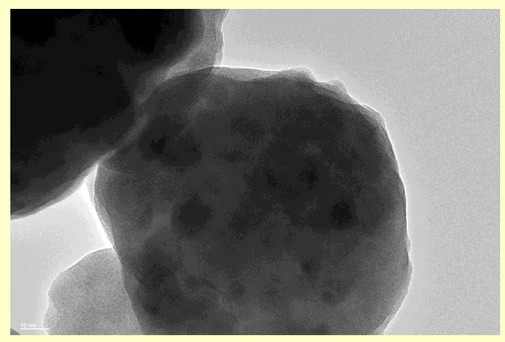
As received sample: spongy aspect with large numbers of pores and voids; average crystallite size about 10 nm. After hating 1h at the temperatures 600C and 900C crystallite grouth was noticed up to 50 nm.

mechanochemical milling

La_2O, $CaCO_3$, MnO_2 were mixed in appropriate molar ratios and milled in in the Fritsch Pulverisete Premium 7 mill. Ratio between mass of starting mixture and balls was 1:20. After only 3h of milling single phase LCMO was obtained. Samples milled 3-15 hours, were additionally heated at several temperatures (300-900C).



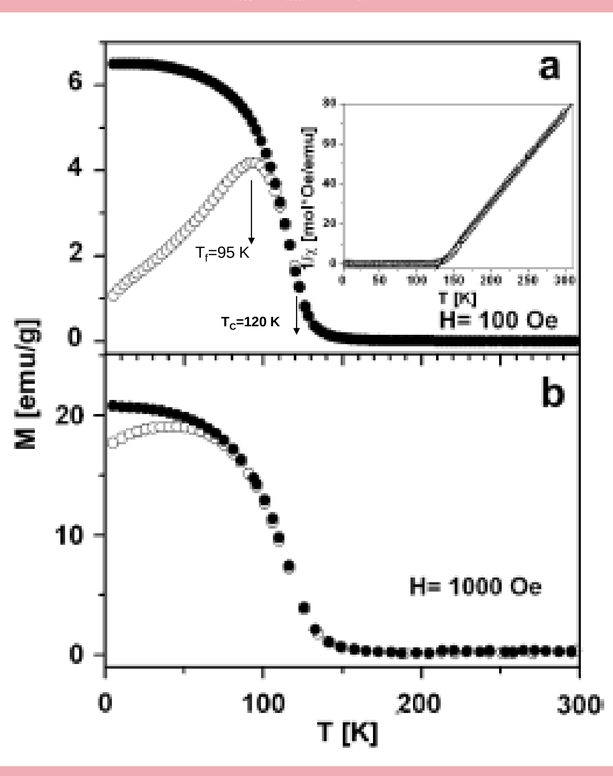


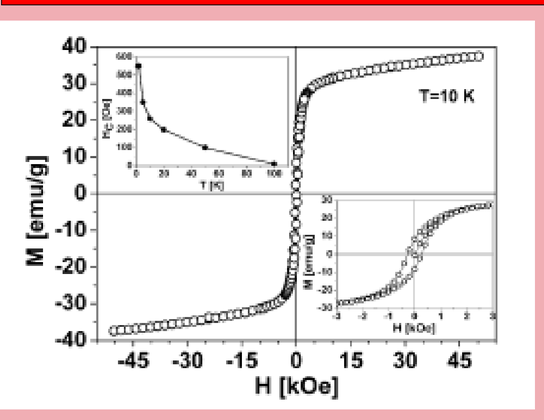


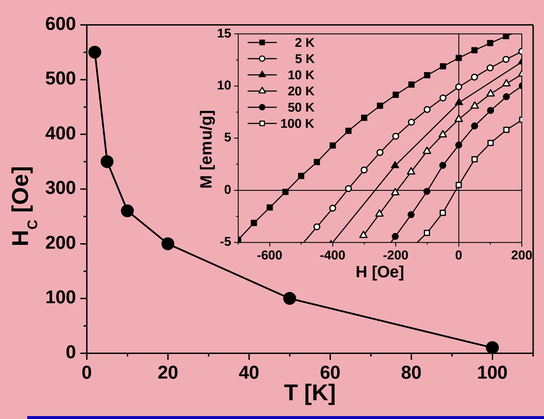
After milling average crystallite size decreases rapidly (for 5h) from 70 nm to 10 nm. In the same time strain was decreasing showing stabilization of structure with prolong milling. After 5h of milling crystallite size and strain remain constant.

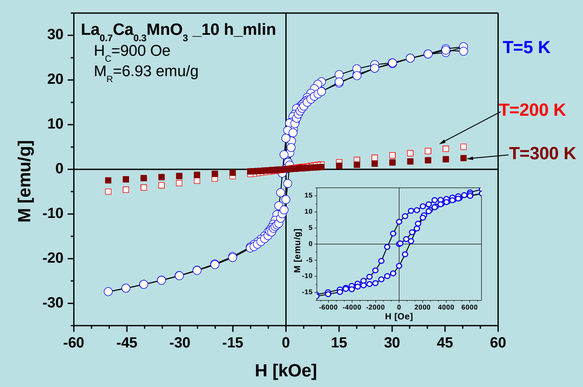
Magnetic measurements:

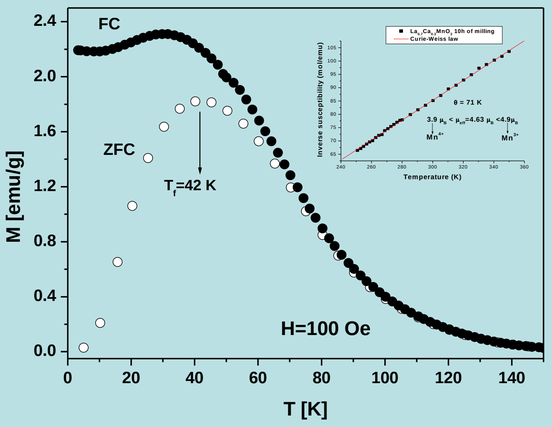
$La_{0.7}Ca_{0.3}MnO_3$ as received

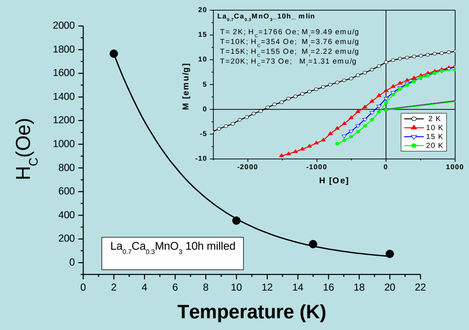


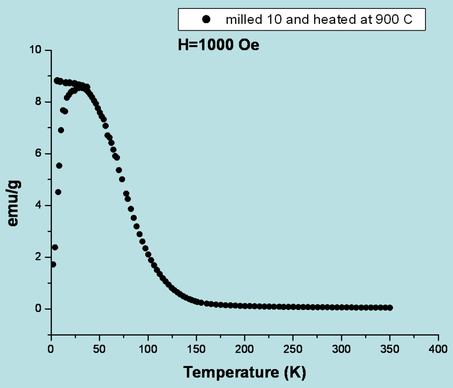




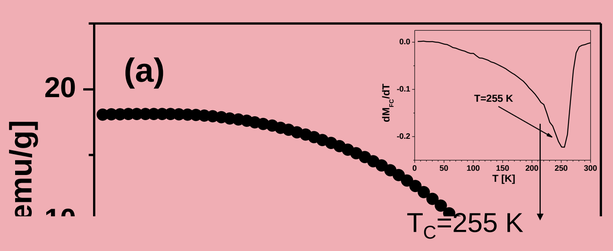


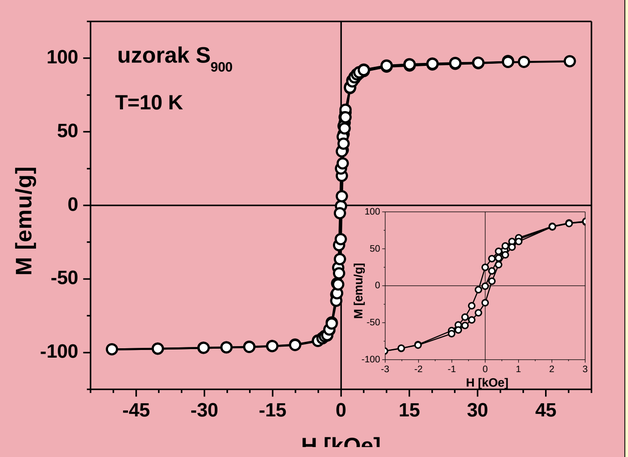


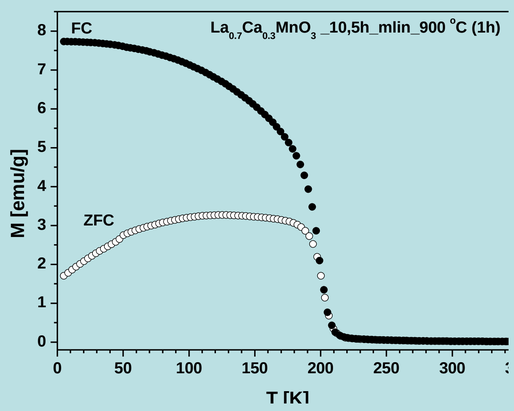


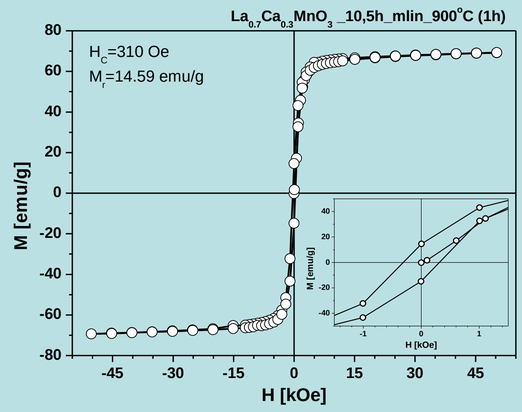


After aditional heat treatment at 900 C:









CONCLUSION: Samples of 10 nm which are obtained after ball milling show higher magnetic anisotropy, which is consequence of introducing much defects during milling procedure. Therefore they show higher coercitivity, smaller saturation magnetization and more pronaunced nanomagnetic characteristics then the samples obtained by glycin nitrate procedure. Thermal treatments can only partialy remove differences in magnetnic bechaviour of samles produced by these two procedures. After termal treatments, samples obtained by ball milling lose their nanomagnetic characteristics and show, insted of spin-glass characteristics, ferromagnetic bechaviour. All these characteristics are quite different then those obtained with the samples produced by glycin nitrate procedure.