Structural and magnetic properties of nanoparticle La0.7Ca0.3MnO3 manganites obtained by mechanochemical procedure

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Mechanochemical procedure was used to produce mixed valence manganite $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) from corresponding metal oxides. The samples were characterized by using X-ray diffraction, transmission electron microscopy and magnetic measurements. The results showed that it is possible to produce single phase LCMO perovskite powders after 3 h of ball milling. Prolonging milling time, up to 15 h, results in decreasing of crystallite size, strain as well as stabilization of crystal structure. DC magnetic measurements, performed in different magnetic fields showed phase transition at temperature T_B which is assigned to blocking temperature of the single domain nanoparticles. M(H) measurements at constant temperature $T<T_B$, exhibit hysteretic curves, showing ferromagnetic character of the sample. The dynamic properties of 10 h ball-milled sample were investigated by AC susceptibility using the Neel–Brown and Vogel–Fulcher model for superparamagnetism. Structural and magnetic properties depending of milling time are discussed, and compared with the similar samples, obtained by different chemical routes.

La0.7Ca0.3MnO3 synthesis characterization:

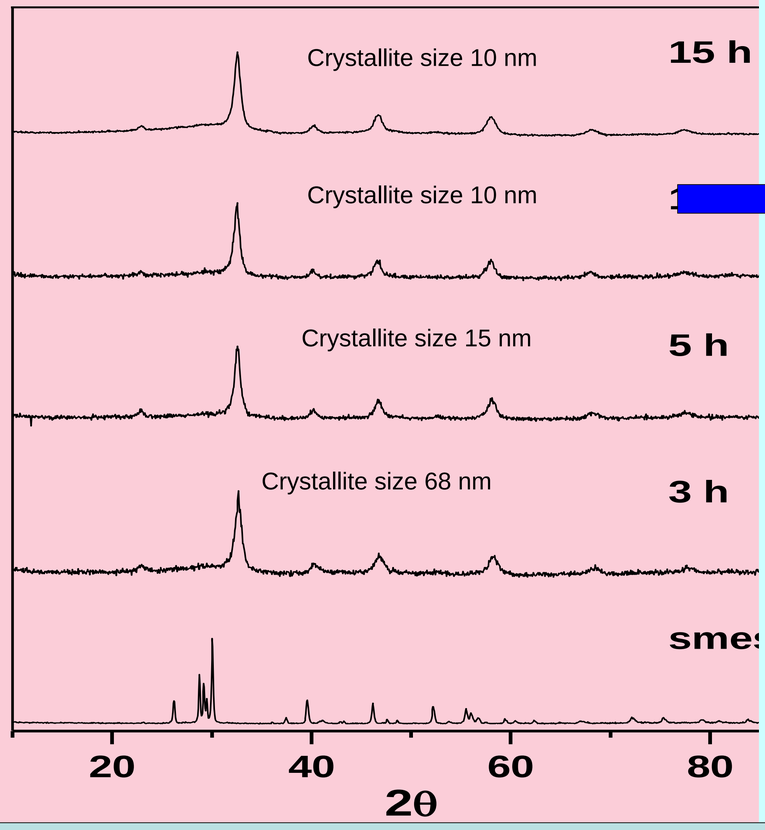
Mechanochemical synthesis:

Milling was performed in the Fritsch Pulverisete Premium 7 mill. Corresponding oxides were mixed in appropriate molar ratios and after every half hour of milling (rpm 1000) crystal structure were controlled by x-ray diffraction. After only 3h of milling single phase LCMO was obtained. After prolonged milling Crystal structure and microstructure (perovskite) was analysed by Rietveld profile method. Samples milled 3-15 hours, were additionally heated at several temperatures (300-900C) and their crystal parameters and magnetic structure were followed.

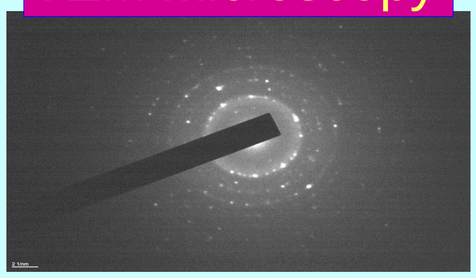
Results: After 3h of milling sample with crystallite size of 20 nm and very high strain is obtained. Milling time of 10 h reduces crystallite size to 10 nm with smaller crystal strain and prolonged milling time live practical constant crystallite size but further crystal strain is obtained.

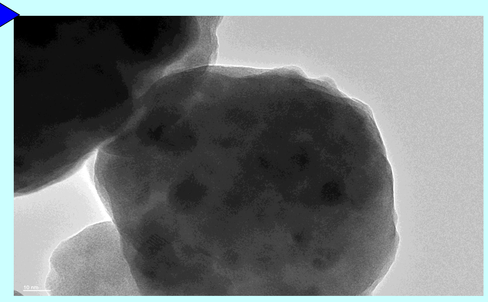
Heating of samples for 1h at different temperatures, leads to increase of crystallinity and crystallite size (up to 30 nm) and further crystal stabilization.

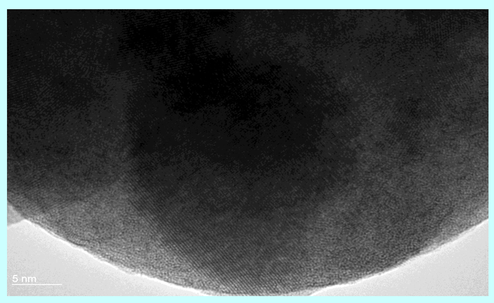
X-ray diffraction



TEM microscopy

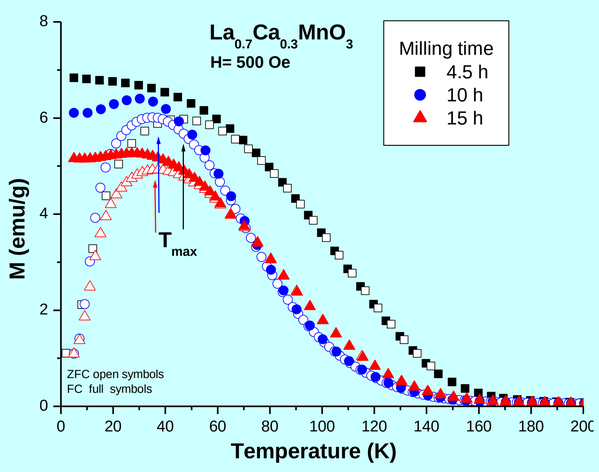


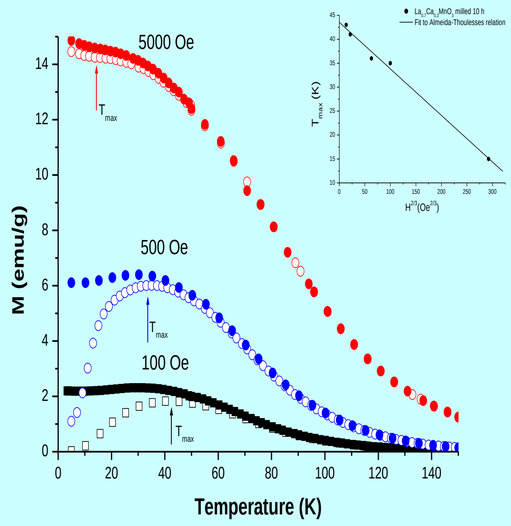


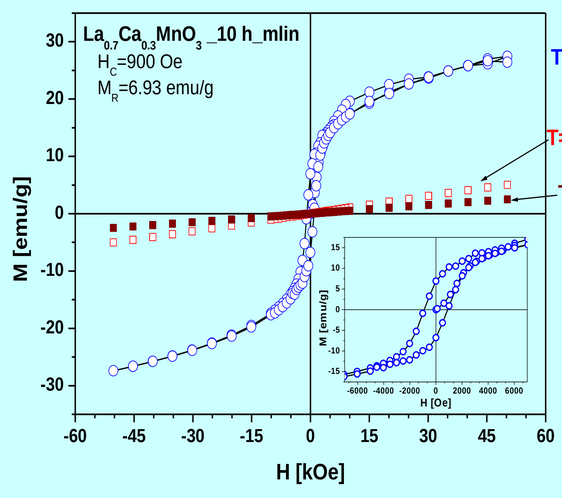


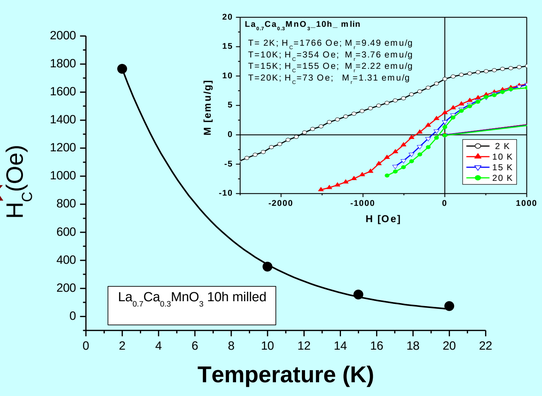
Magnetic measurements:

M(T), M(H) and AC susceptibility measurements were performed at SQUID MPMSXL-5 Quantum Design magnetometer in the temperature range 2K<T<350K and magnetic field 0T<H<5T.

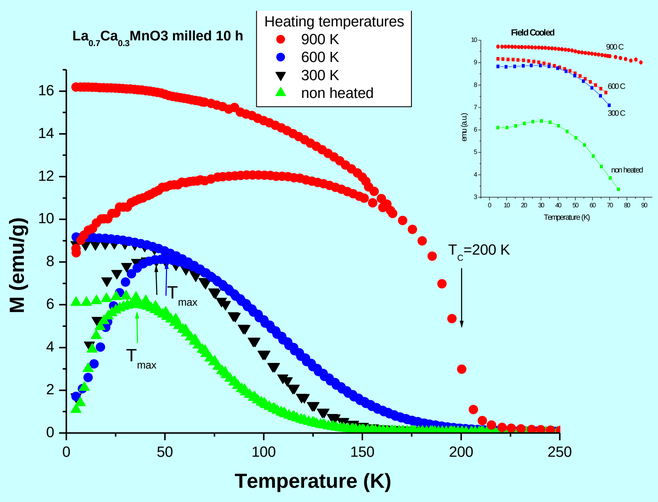


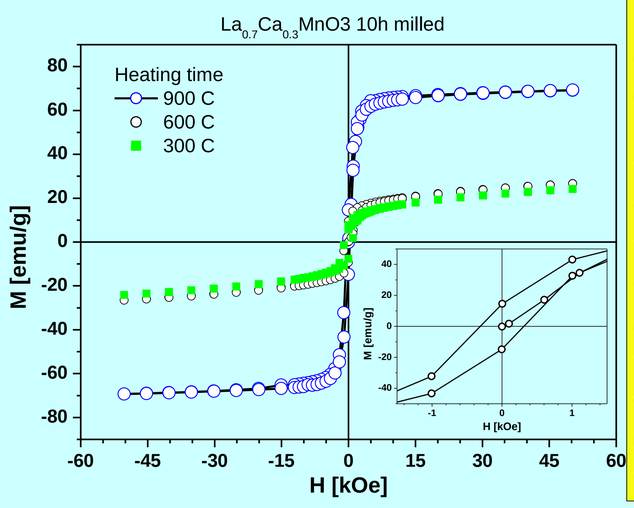






Influence of additional heating





CONCLUSION: Samples of 10 nm which are obtained after ball milling show high magnetic anisotropy, which is consequence of introducing much defects during milling procedure. Single phase was obtained after only 3.5 h of milling. With prolonged milling crystallite size as well as strain first decreasing (up to 5 h of milling) and then both parameters remain constant. Crystallite size decreases with time of milling starting from 65 nm (for 3.5 h) and up to 10 nm after 5h of milling. All milled samples, depending of milling time, show spin glass transition at low temperatures ranging from 30-60 K and high coercitivity up to 2000 Oe. On the other hand saturation magnetization is much lower then those obtained in bulk samples because of introduced defect. Thermal treatments of the samples leads to crystallite size increas acompanig with increas of saturation magnetization and wanishing nanomagnetic characteristics. Samples wich were treated 1h at 900 C show tipical ferromagnetic bechaviour with the Curie transition at 200 K.