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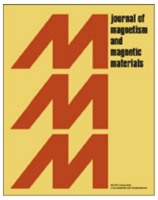

Improved crystallinity, spatial arrangement and monodispersity of submicron $La_{0.7}Ba_{0.3}MnO_3$ powders: A citrate chelation approach

Ch. N. Rao [a], S. Shanmukharao Samatham [b], V. Ganesan [b], V.G. Sathe [b], D.M. Phase [b], S.N. Kale [a,]*

[a] Department of Applied Physics, Defence Institute of Advanced Technology, Girinagar, Pune 411025, India
[b] UGC–DAE Consortium for Scientific Research, Khandwa Road, Indore 452 017, India

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ABSTRACT

The perovskite manganite systems have been the materials of tremendous interest due to their strong correlation between structure, transport and magnetism. These materials in their single-crystal form show colossal magneto-resistance (CMR), but the applied fields are very high (~1–5 T). The polycrystalline samples do show high low-field magneto-resistance (LFMR), but good amount of control over particle sizes and grain-boundary distribution is required, which is well known but less realized in practical approaches. In this context, we report on synthesis and manipulation of polycrystalline $La_{0.7}Ba_{0.3}MnO_3$ (LBMO) submicron powders using citric acid chelation. The Citrate-gel route is used to synthesize poly-dispersed LBMO powders which are subjected to citrate chelation for a duration of 0 (LB0) to 4 h(LB4) . The samples show improved ordering in X-ray diffraction patterns. Raman spectroscopy scans indicate changed mode signatures due to the probable chelating process, which alters the surface morphology. X-ray photoelectron microscopy shows an evidence of fine citrate layer on the grain boundaries. Low temperature *B–H* curves exhibit fine hysteresis loops for all samples, while room temperature *B–H* curves shows paramagnetic response. Scanning electron microscopy images showed the formation of well arranged, connected, mono-dispersed grains of LB4 sample, as against polydispered LB0. The magneto-resistance (at $H=100$ kOe) is seen to enhance for LB4 at its transition temperature (75%, as compared to LB0, where it is 60%), which can be attributed to the well-controlled inter-grain tunneling phenomenon and thin insulating regions in between, created due to citrate chelation, which probably enhances the scattering phenomenon and its susceptibility to applied fields. As citric acid is known to chelate Mn ions, it probably chelates the smaller LB particulate structure and leaves behind citrate-connected submicron grains of LBMO, which are seen to be well engineered.

1. Introduction

Devices that rely on electron's spin to perform their functions form the foundation of spintronics or magnetoelectronics [1–4]. Such spintronic devices are being developed for applications such as ultrasensitive magnetic sensors and magnetoresistive random access memory (MRAM). In this context, the perovskite manganites of general formula $R_{1-x}A_xMnO_3$ (R=rare earth, A=Ca, Sr, Ba and Pb) have drawn considerable attention, especially following the discovery of colossal magnetoresistance (CMR) [5,6]. Mixed valence manganites offer a good degree of compositional flexibility which enables the manipulation of oxide structure electronic and magnetic properties. It has been documented that large negative magnetoresistance effects appear near and below the Curie temperature. The mixed-valence oxides can be considered as a range of materials between end members such as $LaMnO_3$ and $CaMnO_3$ with formal valence states La^{3+} Mn^{3+} $3O^{2-}$ and Ca^{2+} Mn^{4+} $3O^{2-}$, leading to mixed-valence compounds such as $(La^{3+}_{1-x}Ca^{2+}_x)$ $(Mn^{3+}_{1-x}Mn^{4+}_x)O_3$. The nominal electronic configurations of Mn^{3+} and Mn^{4+} are $3d^4$ and $3d^3$ respectively. Each of the end members is antiferromagnetic and insulating, but the compositions in between cover a wide range, e.g. for $x\sim0.3$ the samples are ferromagnetic and conducting. Structurally, the system is characterized by the wide range of cations which can occupy the A site in the perovskite structure, which may be set at the body-center or the cube corner. A good way to model the structure is as a cubic close-packed array formed of O^{2-} anions and large A cations, with the small B cations in the octahedral interstitial sites. The ideal cubic structure is distorted by cation size mismatch and the *Jahn–Teller effect*, whereby a distortion of the oxygen octahedron surrounding the B site cation splits the energy levels of a 3d ion such as Mn^{3+},

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* Corresponding author.
E-mail address: sangeetakale2004@gmail.com (S.N. Kale).

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thus lowering the energy. The distorted structures are frequently orthorhombic. Divalent cations which can occupy the body-center A site include calcium, barium, strontium and lead; trivalent cations include yttrium, lanthanum, praseodymium, neodymium and some other rare earths (R). Since the observation of colossal magnetoresistance (CMR) close to T_c in good quality single crystals and epitaxial films of doped manganite perovskites generally requires large applied magnetic fields, it has severely restricted their applicability [7–10]. Hence for applied aspects, occurrence of significant MR at low applied magnetic fields and at room temperature would be required.

A number of subsequent studies, both on bulk and thin film samples, have confirmed the important role of grain boundaries on the MR behavior of manganites because of their enhanced MR at small fields (low field magnetoresistance, LFMR) on the order of a few mT [9–14]. In this context, unlike the single crystal, polycrystalline samples exhibit a sharp drop in the resistance at low fields followed by a slower background negative MR at higher fields. In contrast to the resistivity variations, the magnetization data are very similar to that for the single crystal. This suggests that the MR in the polycrystalline samples is dominated by intergrain effects, with the magnetic field associated with the sharp drop in resistance identical to that associated with magnetic domain rotation. As has been argued by Sun and Gupta [14], disruption of crystalline order in the manganites at the grain boundaries is sufficient to induce a local spin disorder that results in a large low-field MR component, especially at low temperatures. Using grain boundaries to manipulate magnetic behavior thus proves to be a simple method to significantly improve the low-field sensitivity of these materials. Different growth techniques, such as sputtering [15,16], electron beam/thermal co evaporation [17,18], metal–organic chemical vapor deposition (MOCVD) [19], pulsed laser deposition [7], nebulizer spray pyrolysis [20] and the sol–gel technique [21] have been extensively used for deposition of manganite thin films. With the advent of the nanocrystalline forms of various materials, manganite systems have also seen changes in synthesis approaches. Chemical routes assisted with various surfactants have been utilized by various groups to achieve low-temperature manganite phase formations. The physical properties of manganites, so formed, are also expected to depend on material size due to both the nanoscale phase inhomogeneities inherent to these materials and additional surface effects. Hwang et al. [9] pointed out that the large LFMR of the polycrystalline samples is dominated by spin polarized tunneling between neighboring grains. This is quite different from their single crystals and epitaxial films counterparts, where the double exchange mechanism is prominent. These synthesis methods have not been appropriate for many advanced applications, due to their grain boundary engineering incapability. The sensor specifications cannot be optimized, though at research level, the techniques show significant promises.

In this context, we report on a different approach to synthesize monodispersed, submicron-sized particles from bulk, micron-sized polydispersed manganite particles using a chemical approach. The Gel route has been employed to synthesize micron sized $La_{0.7}Ba_{0.3}MnO_3$ (LBMO) particles which have been chemically treated to tune the particle size and engineer the spatial arrangement using a citrate-chelation approach. Samples have been studied as a function of chelation time from 0 h to 4 h (labeled as LB0, LB1, LB2, LB3 and LB4). A controlled chelation of LBMO particles has been observed in our studies with sequential and stoichiometry-maintained particle chiseling. It was observed that smaller particles chelate out easily and submicron sized particles are left behind, which are uniform in size, after a duration of about 4 h. Sequential weight loss was observed as the sample went through LB0–LB4. An interesting change in surface morphology was observed and surface defects seem to get regularized with chelation with the citrate groups primarily attacking the metal ions and getting associated at the grain boundaries of LBMO. As these particles (LB4) were pressed in pellet forms and were subjected to magnetoresistance studies, comparatively low-field (100 kOe) magneto-resistance was seen to be enhanced for LB4 at its transition temperature (75%, as compared to LB0, for which it is 60%). X-ray diffraction (Philips PW 1710 diffractometer, XRD), Raman spectroscopy, and X-ray photoelectron spectroscopy (PES beamline on Indus-1 Synchrotron source, XPS) have been used to confirm the structure, structural changes and elemental analysis. Vibrating sample magnetometry (EG&G, USA, PAR 4500, VSM) has been employed to study the temperature and field dependent magnetization of the samples. Simulated thermogravimetric analysis (S-TGA) was used to monitor the weight loss as a function of chelation time. Scanning electron microscopy (Leica Cambridge 440 microscope, SEM) has been used to observe the morphological modifications and a four-probe resistance measurement system (PPMS) was employed to measure the resistance change as a function of applied field.

2. Experimental

To prepare a crystalline LBMO compound, the sol–gel method was used [22]. A mixture of 7 mmol Lanthanum acetate ($C_6H_9LaO_6$, 97% Aldrich), 3 mmol Barium acetate($C_4H_6BaO_4$, 98.5% Aldrich) and 10 mmol Manganese acetate tetra hydrate ($C_4H_6O_4 \cdot 4H_2O$, 99.5% Aldrich) was used as the precursor of the reaction. La, Ba, Mn acetates were weighed in accordance with the cation order La: Ba: Mn = 0.7: 0.3: 1 and thoroughly mixed. Proper stoichiometric quantities of these compounds were dissolved in minimal amount of water to give the composition $La_{0.7}Ba_{0.3}MnO_3$. This solution was mixed with citric acid solution in 1:1 volume ratio. Then 28 ml HNO_3 (concentrated 70%) was added to the solution drop-by drop under constant stirring. The solution was held in a water bath at 100 °C. A yellowish transparent gel was formed on complete evaporation of water. The obtained gel was put in a furnace, which was pre-heated at 100 °C for complete drying. The powder obtained by crushing these flakes was heat-treated at temperatures of 200 °C, 400 °C, and 600 °C for 1 h, 2 h and 4 h respectively. The final sintering was performed at 800 °C for 6 h in an electrical furnace (Model BIT-40). The heating and cooling rate for sample in the furnace was maintained to be 5 °C/min using an in-built temperature controller of the furnace. The foamy precursor decomposed to give very light, homogeneous, black-colored flakes of extremely fine particle size. This sample was labeled as LB0.

The ratio of LB0 powder to citric acid 1:6 when taken in deionised water, and was kept on a shaker for 2 min. This mixed chemical component was ultrasonicated (BIO-Technics, India) at room temperature for different time intervals between 0and4 h. After every hour, the reaction was stopped and the chelated LBMO (portion of remaining LBMO powder at the bottom of the beaker, which was carefully extracted using a magnetic separation) was washed with ethanol and dried at 60 °C in an oven. The samples were labeled according to the chelation time in hours as LBO, LB1, LB2, LB3 and LB4. These powder samples were used for characterization. The magneto-resistance as a function of magnetic field was measured by employing the four probe technique using a current source, nanovoltmeter and a temperature-controlled sample holder. The sample was kept in varying magnetic field 0–1 T and measurements were done either at fixed temperature (and varying fields) or at varying fields (and fixed temperature).