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Short communication

Synthesis of $La_{0.7}Sr_{0.3}MnO_3$ at 800 °C using citrate gel method

V. Ravi [a,*], S.D. Kulkarni [b], V. Samuel [c], S.N. Kale [d], J. Mona [d], R. Rajgopal [d], A. Daundkar [d], P.S. Lahoti [e], R.S. Joshee [e]

[a] *Physical and Materials Chemistry Division, National Chemical Laboratory, Pune 411008, India*
[b] *Centre for Materials Characterization, National Chemical Laboratory, Pune 411008, India*
[c] *Catalysis Division, National Chemical Laboratory, Pune 411008, India*
[d] *Department of Computer Science, Fergusson College, Pune 411004, India*
[e] *Department of Physics, Fergusson College, Pune 411004, India*

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Abstract

Manganite systems have been of considerable interest in the recent past due to their potential to operate in wide property range and also to serve as effective magnetic sensing and storing devices when synthesized using stringent conditions. We report a novel citrate gel method, in which $La_{0.7}Sr_{0.3}MnO_3$ system has been synthesized at temperature 800 °C (LSMO800) with the synthesis duration is 6 h. The results have been compared with the sample synthesized at 1050 °C (LSMO1050). The synthesized bulk polycrystalline sample shows single-phase nature with the increase in particle size from ~50 nm to 300 nm with the increase in the sintering temperature. The magnetization data for LSMO800 shows well-defined hysteresis with saturation magnetization at around 1800 Oe and Curie temperature at 360 K, which is slightly lower than that of LSMO1050, which is 375 K. The results can be well attributed to the grain boundary effects.

Keywords: Ceramics; Oxides; CMR; Citrate gel method

1. Introduction

Colossal magnetoresistive (CMR) materials are doped Mn-oxides with generalized formula as $(R_{1-x}M_x)MnO_3$ (where R = La, Nd like rare earth element and M is a divalent dopant such as Sr and Ca). These materials exhibit large magnetoresistanc and have wide applications as magnetic sensors, hard disk read–write heads, infrared detectors and microwave based application [1–3]. The materials are of immense interest due their rich phase diagram, which indicate that their properties are highly dependent on the type of R and M and also on the value of x [4–6]. The parent compound ($LaMnO_3$) is an antiferromagnetic insulator, while the hole doped manganites undergo metal–insulator transition and ferroparamagnetic transitions at T_c and T_p respectively, where T_c is close to T_p. By changing the doping concentration, the electrical and magnetic properties can be tuned as per the specific device requirement. There have also been reports on their wide range of properties, which depend on the grain size of the synthesized sample. After significant studies, it has been observed that if the manganite material consists of grain boundaries, the materials exhibit large magnetoresistance at sufficiently low magnetic fields [5,12]. Understanding of transport and magnetotransport properties in these materials is an appreciable challenge. Of all various kinds of manganite systems, $La_{1-x}Sr_xMnO_3$ (with $x = 0.3$) (LSMO) is one typical composition, which is of much interest due to its T_c much above room temperature (~350 K) and substantial magnetoresistance (MR) [4,7–9].

These materials have been around for almost a decade now, and various synthesis routes have been investigated to form these compounds in their bulk as well as thin film form. The magnetic and magneto-transport properties of these materials are highly sensitive to the synthesis route, pre- and post-synthesis annealing, calcinations and sintering temperatures, oxygen stoichiometry control, grain boundary engineering and so on. Synthesis time, temperature range, quality of the precursors used and consideration of their economical production viability at larger scale, are the major issues, which are to be worried about. Further, the sample synthesized should be homogeneous, with smaller particle size, compact and hard,

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* Corresponding author. Tel.: +91 20 5893300; fax: +91 20 5893044.
E-mail address: r.venkat@ncl.res.in (V. Ravi).

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if it has to be further used for thin film deposition. Solid-state reaction route has been used quite intensely [4,7,9,10], which gives bulk polycrystalline samples. The synthesis temperature is around 1400–1700 °C with the calcinations and sintering time totals to about 48 h. This route utilizes the precursors, which are less expensive oxides and hence the procedure is economical. Sol–gel method [11], glycine nitrate combustion [12], flash-pyro phosphoric acid [13] and chemical methods [7] are also few other routes used, which, have been utilized by various research groups to synthesize bulk samples. Solid-state reaction route, though is economical, is time consuming and requires very high temperature for proper phase formation. Sol–gel technique gives advantage over solid-state reaction route in terms of time and temperature and quality of the samples so formed. In these methods, the precursors used are normally organo-metallic solvents, which are fairly expensive. The methods use lower temperatures and the synthesis time is in the range of about 16 h. In this context, we report simple citrate gel method to synthesize high quality LSMO bulk samples. The samples are synthesized using basic element acetates and the synthesis time is of the order of 6 h. This route is, hence, highly time efficient and economical to synthesize complex compounds. We synthesized LSMO at 800 °C (LSMO800) and it has been observed that grain size is about 50 nm for the single-phase polycrystalline LSMO sample. We observe the ferromagnetic transition temperature to be 360 K, which is the typical transition temperature recorded for the LSMO sample of given stoichiometric ratios. For comparison, we have also synthesized sample at 1050 °C (LSMO1050) and it is seen to have grain size ~300 nm, with the ferromagnetic transition temperature at 375 K. Conventional characterization techniques have been employed to explore the structural and magnetization data.

2. Experimental

Lanthanum acetate hydrate, strontium acetate hydrate and manganese (II) acetate tetra hydrate were used as precursors in this method. Proper stoichiometric quantities of these components were dissolved in minimal amount of water to finally give the composition $La_{0.7}Sr_{0.3}MnO_3$. This solution was mixed with citric acid solution in 1:1 volume ratio. Small amount of nitric acid (~1/5th quantity of water) was also added to convert the corresponding precursors into their respective nitrates. On heating this mixture on a water bath at 350 K, a yellowish transparent gel was formed on complete evaporation of water. Continued heating caused the gel to swell and fill the beaker with a foamy precursor. Further subjecting it to a temperature of 700 K for about 2 h, the foamy precursor decomposed to give very light, homogenous, black-colored flakes of extremely fine particle size. From the powder obtained by crushing these flakes, pellets of 1 cm diameter were prepared using a hydraulic press and applying a pressure of 10 MPa. The pellets were subjected to final sintering temperature of 800 °C or 1050 °C for duration of 2 h to yield LSMO800 or LSMO1050 samples, respectively. X-ray diffraction technique (Philips PW 1710 diffractometer), and scanning electron microscopy (Leica Cambridge 440 microscope) have been used to study the structural details and to know the grain size of the bulk polycrystalline pellet form-sample. Vibrating sample magnetometry (EG & G, PAR 4500 model) has been employed to study the magnetization of the prepared sample.

3. Results and discussion

The samples are highly dense (sinter-density ~92% of theoretical value) and uniform. Fig. 1 shows the X-ray diffraction pattern of both the samples. It shows typical polycrystalline nature with the indication of phase formation [13]. The careful examination of the two xrds reveal that the LSMO800 shows slight peak broadening as compared to the LSMO1050 sample. Fig. 2 shows the SEM micrograph of the LSMO800 and LSMO1050 pellet. The particle size for LSMO800 is seen to be ~50 nm, which is the best as reported so far, according to our knowledge. The particle size for LSMO1050 is of the order of 300 nm. The micrographs distinctly show growth of grains with the increase in sintering temperature. Fig. 3 shows the graph of magnetisation versus temperature taken at 100 Oe. This shows clear ferromagnetic transition at 375 K for LSMO1050 which is also in agreement with the reported values [9–13]. LSMO800 shows this transition at 360 K with the region in between 300 K and

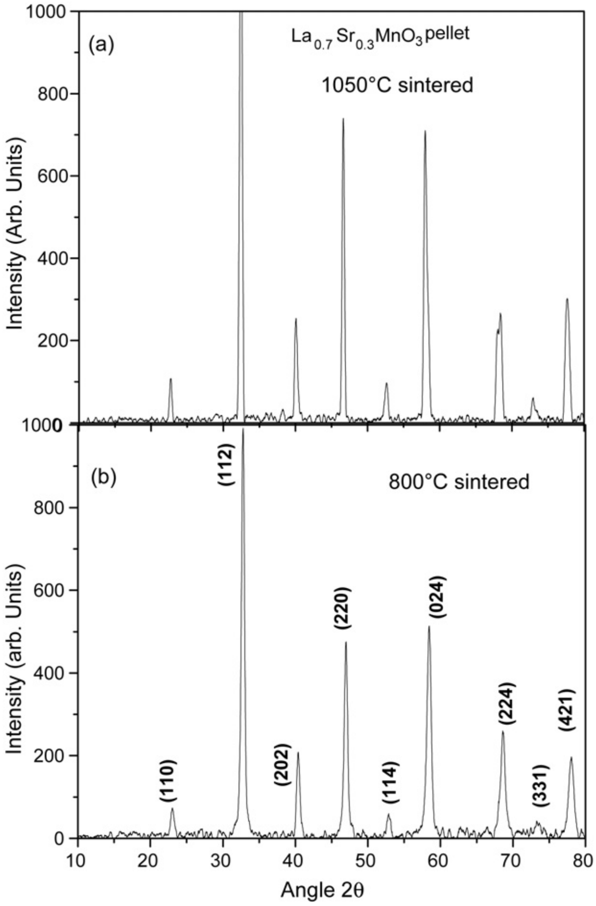

Fig. 1. X-ray diffraction pattern of the sample. It shows typical polycrystalline nature with the indication of polycrystalline phase formation.

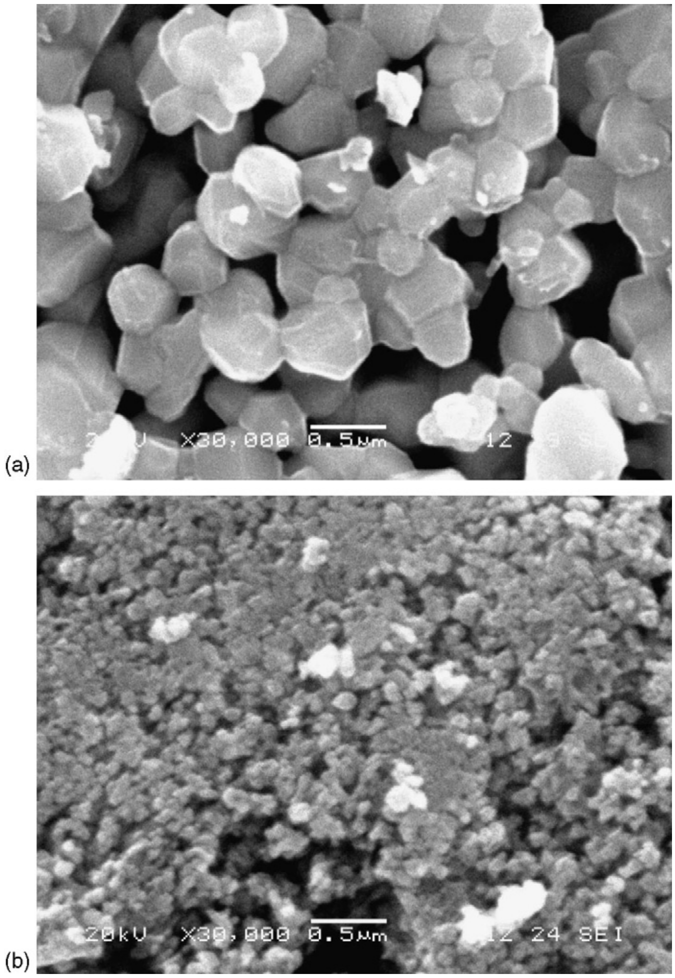

Fig. 2. SEM micrographs of the fracture surfaces of LSMO800 and LSMO1100 samples.

350 K quite blunt as compared to the LSMO1050 sample. The inset of Fig. 3 shows the magnetization data of the LSMO800 sample taken at room temperature. It shows a clear hysteresis with low coercivity and saturation magnetization at around 1800 Oe. The moment (emu/g) matches well with the earlier reported values [4,8].

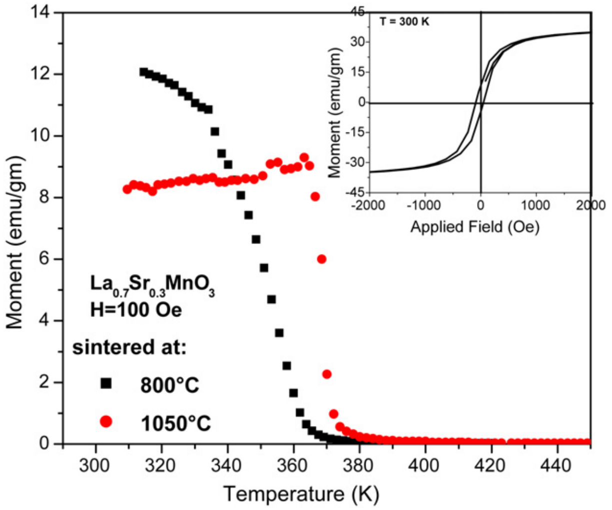

Fig. 3. Magnetizations of LSMO800 and LSMO1100 samples vs. temperature at 100 Oe.

The explanation of the underlying phenomenon may depend on the careful analysis of the magnetism on the surface of the nanostructured magnetic grain. As seen from our results, the magnetic phase transition temperature gradually broadens and shifts to lower temperature as the grain size decreases. This means that magnetic surface effect exists in these granular samples. Earlier studies reveal that coupling among magnetic ions at the surfaces is much weaker than that in the cores due to the coexistence of a large number of dangling bonds and non-coordination of atoms at the surface [14,15]. The lattice structure on the surface is rather amorphous [16] and the magnetic configuration of such material is very much sensitive to the structure [17,18]. Thus, the magnetic configuration of the perovskite on the grain surfaces can be expected to be more chaotic than that in the cores at a given temperature.

The basic characterization of the samples, hence show that the samples synthesized using simple citrate gel method yields high-quality polycrystalline bulk samples in much smaller time frame and at much lower operating temperature. The samples are dense, uniform and of much better quality than the conventional routes. The synthesis route gives a good control over the grain size, and hence the property range which one is looking for, in the given manganite system. This work opens new avenues of studying the doping effects of transition metal ions on the, magnetic and magneto-transport response of such polycrystalline samples. This work is currently being done.

4. Conclusions

We have synthesized LSMO nanoparticles by a simple citrate gel method. The phase formation takes place at 800 °C and particle size increases with increase in sintering temperature. The synthesized samples exhibit well-defined hysteresis curve with magnetization saturation at 1800 Oe and Curie temperature ~360 K.

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