Magnetoresistance studies on barium doped nanocrystalline manganite


Abstract

An energetically attractive, simple, fast and a novel low temperature (300 °C) solution combustion route for the synthesis of crystalline and homogeneous nanoparticles of lanthanum barium manganese oxide La$_{0.9}$Ba$_{0.1}$MnO$_3$+$\delta$ (LBMO) is reported. Formation and homogeneity of the solid solutions have been confirmed by powder X-ray diffraction (PXRD) and energy dispersive X-ray analysis (EDS) respectively. The Rietveld analysis shows both as-formed as well as calcined samples are in cubic phase with space group $\text{Pm}$3$m$. The microstructure and agglomerated particle size of the compounds are examined by scanning electron microscope. Infrared spectroscopy revealed that both Mn–O–Mn bending mode and Mn–O stretching mode are influenced by calcination temperature. The magnetoresistance measurement on sintered LBMO pellet exhibits a broad metal–insulator transition ($T_M$–I) at around 228 K. At 1 T applied magnetic field, LBMO shows magnetoresistance (MR) of 10%, whereas for 4 and 7 T, the negative magnetoresistance values are in the range 51 and 59% respectively at $T_M$–I. The experimental resistivity data of the present investigation are fitted to a simple empirical equation in order to understand conduction mechanism in this compound.

Keywords: Magnetically ordered materials; Chemical synthesis; Magnetoresistance; X-ray diffraction

1. Introduction

Nanoscopic materials consisting of particles uniform in size and shape have been attracting increasing interest for their unique physical and chemical properties and potential technological applications. Indeed, in order to reproducibly manufacture various materials of controlled properties like magnetic, optical, electric, structural, it is essential to use well-defined dispersed powders as precursors [1,2]. It is of interest to study nanocrystalline manganites with particle sizes comparable with magnetic domain sizes in order to better understand the mechanism for the colossal magnetoresistance (CMR). Indeed, nanocrystalline manganites have a higher magnitude of the low-field magnetoresistance (LFMR) as compared to ceramic samples [3]. The discovery of the CMR in mixed manganese oxides RE$_{1-x}$A$_x$MnO$_3$ (where RE is a trivalent rare-earth element and A is the divalent cation) has been a subject of study in recent years. These materials have very interesting electrical and magnetic properties, and also have potential applications for magnetic recording, magnetic switches and magnetic sensors [4–7]. These compounds are Mn$^{3+}$ rich and doping of divalent atoms introduces mixture of Mn$^{3+}$ and Mn$^{4+}$ ions. The mixed valency of Mn ions plays a major role in double exchange (DE) ferromagnetic interaction coupled with metallic resistivity [8–10]. In this, there is an exchange of electrons from neighboring Mn$^{3+}$ to Mn$^{4+}$ ions through oxygen when their core spins are parallel and hopping is not favored when they are anti-parallel. However, this mechanism alone cannot explain all the details of CMR effect. Therefore, other theories have been developed, which besides DE mechanism also incorporate the Jahn Teller character of Mn$^{3+}$ ion by a variable electron–phonon coupling [11].

The properties of hole doped manganese are usually dependent on their preparation routes. Hwang et al. [12] pointed out that the LFMR of the polycrystalline manganites is mainly due to spin polarized tunneling between grains, which is quite different from those observed in a single crystal. Hence, the nanoscaled particles may lead to some more interesting transport and MR...
properties than bulk materials. These manganites are usually prepared either by the ceramic route [13] or wet chemical methods like co-precipitation, sol-gel and hydrothermal. The ceramic route needs higher temperature and requires long annealing time to get homogeneous composition and desired structures where as most of the wet chemical methods find several disadvantages. These methods require long processing time, costly chemicals, and special experimental set up, long sintering or annealing process to get desired product. In contrast, the solution combustion process finds several advantages like fast heating rates, short reaction time, besides produces porous, foamy and nanoscaled product. In fact high purity and homogeneity are achieved at temperature as low as 300 °C as against 1470 °C needed to synthesize these materials using ceramic route [14,15]. La1-xBaxMnO3 compounds have been less studied compared to the La1-xCaxMnO3 and La1-xSr1MnO3 systems. This is probably due to the difficulty in substitution of relatively large Ba2+ for La3+ ion in LaMnO3. In the present work, we explore the possibility to extend the novel combustion process for the preparation of rarely studied barium doped manganite at low temperature and the combustion derived products are characterized by various techniques. The MR measurements are carried out using four-probe method in a liquid helium cryostat.

2. Experimental

2.1. Chemicals

The fuel oxalyl dihydrazide C2H6N4O2, ODH was prepared using hydrazine hydrate and diethyl oxalate as reported in the literature [16]. Lanthanum nitrate La(NO3)3·4H2O, manganese nitrate Mn(NO3)2·4H2O and barium nitrate Ba(NO3)2·4H2O were used as oxidizers. The stoichiometry of the redox mixture used for the combustion has been calculated using the total oxidizing and reducing values of the compounds which serve as numerical coefficients for the stoichiometric balance so that the equivalent ratio (δe) is unity and the energy released by the combustion is maximum. The detailed calculation of stoichiometry has already been reported [17–19].

2.2. Synthesis of LBMO

The stoichiometric amounts of lanthanum, manganese and barium nitrates and ODH are mixed in a minimum quantity of double distilled water. The solution mixture is concentrated by heating it in a Petri dish on a hot plate until excess free water evaporated and wet product is obtained. Then the Petri dish is introduced into a muffle furnace maintained at 300 ± 10 °C. Initially, the wet powder thermally evaporated and followed by decomposition with large amount of gases. The combustion is self-propagating, within a few minutes, the reaction is completed and fluffy LBMO powder is obtained. Assuming complete combustion, the equation for the formation of sample can be proposed as follows:

\[ 3.6 \text{La(NO}_3\text{)}_3(\text{aq}) + 0.4 \text{Ba(NO}_3\text{)}_2(\text{aq}) + 4 \text{Mn(NO}_3\text{)}_2(\text{aq}) + 9.8 \text{C}_2\text{H}_6\text{N}_4\text{O}_2(\text{aq}) \]
\[ \rightarrow 4 \text{La}_0.9\text{Ba}_{0.1}\text{MnO}_3(\text{s}) + 19.6 \text{CO}_2(\text{g}) + 29.5 \text{H}_2\text{O}(\text{g}) + 29.5 \text{N}_2(\text{g}) \]
\[ 19.6 \text{moles of gases} \]  

The product obtained by combustion process is usually porous and fine foamy because of large number of gaseous products like H2O, CO2 and N2 are releasing during reaction. The number of moles of gaseous products releasing during reaction affects the product very much. In fact as the number of moles of gases liberating during combustion reaction increases the fire retention time and exothermicity of the reaction.

2.3. Characterization

To qualify the structure, X-ray patterns are obtained with a Philips X-ray diffractometer using Cu Kα radiation with a nickel filter. The elemental analysis and homogeneity of samples are investigated by means of quantitative energy dispersive spectroscopy (EDS). The FTIR spectral studies have been performed on a Perkin-Elmer spectrometer (spectrum 1000) with KBr pellets. Quantal Chrome Corporation, NOVA 1000 Gas Sorption Analyzer, determined the surface area of the powder sample. Rietveld analysis program Fullprof method [20] and Debye–Scherrer’s [21] formula are used to evaluate the lattice parameters and crystallite sizes respectively. The MR measurements were performed on sintered palletized sample using four-probe method in a liquid helium cryostat (Janis Supravatemp Cryostat) vary from 300 K down to 70 K with magnetic field vary from 0 to 7 T, using super conducting magnet.

3. Results and discussion

3.1. Powder X-ray diffraction

Fig. 1 shows PXRD of as-formed and calcined (900 °C, 6 h) LBMO samples. The crystal structure and lattice parameters have been evaluated by the Rietveld analysis program Fullprof method [20]. As-formed and calcined LBMO manganites are indexed in cubic symmetry (Pm3m). The broad characteristic of the XRD pattern reveals that the nanocrystalline nature of the combustion derived products The existence of strong oxidizing atmosphere at elevated temperature during combustion reaction leads to excess of Mn4+ (>30%) in as-formed and in calcined (900 °C, 6 h) LBMO samples stabilizing the cubic phase. As it clearly seen in calcined sample (inset of Fig. 1), there is a decrease in the full width at half maximum (FWHM) and shifting of diffraction peak (1 1 0) towards the lower angle confirms the increase in crystallite size. The average particle size of LBMO manganites was estimated from the full width at half-maximum (FWHM) of the diffraction peak of the powders using Scherrer’s formula [21]. In the present work, the crystallite size of the manganites is around ∼45 nm. Fig. 2 shows the Rietveld fit to
the PXRD data taken for calcined LBMO sample. The structural parameters of calcined LBMO sample evaluated by standard Rietveld technique [20] are found to be: \( a = 3.891 \, \text{Å} \), with a unit cell volume \( V = 58.924 \, \text{Å}^3 \).

### 3.2. Effect of Mn\(^{4+}\) content

Many studies indeed suggest that the ratio of Mn\(^{3+}\)/Mn\(^{4+}\) is a key component for understanding magnetic and transport properties [22]. It is observed that combustion derived samples show higher percentage of Mn\(^{4+}\) content compared to the samples prepared via ceramic route. When the concentration of Mn\(^{4+}\) ions increases, there is a corresponding increase in the oxygen content, so the \( \text{La}_{0.9}\text{Ba}_{0.1}\text{MnO}_3+\delta \) formula can be written as \( \text{La}_{0.9}\text{Ba}_{0.1}\text{MnO}_3+\delta \) (where \( \delta \) indicates the excess oxygen). Van Roosmalen et al. [23] concluded that the randomly distributed cation vacancies in equal amounts in perovskites lattice is responsible for excess oxygen in hole doped manganites. The Mn\(^{4+}\) content in combustion derived LBMO samples was estimated from the iodometric titration [24] and it is found that the Mn\(^{4+}\) content is 36 and 32\% for as-formed and calcined samples, respectively.

### 3.3. Measurement of surface area

The combustion derived powders generally show a large surface area and were weakly agglomerated. This may be due to the large amounts of gas evolved during combustion and to the high \textit{in situ} temperature. In fact the liberation of gaseous products produced during combustion, agglomerates disintegrate and more heat is carried away from the system, thereby hindering the particle growth, leading to high surface area and creating porous (voids) regions. The surface area is one of the important parameters used to characterize powder samples. The surface area (m\(^2\)/g) is related with other parameters such as particle size, shape and density. The BET surface area determination involves admitting nitrogen as an adsorbing gas to a known weight of sample [25]. As-formed LBMO has surface area of about 34 m\(^2\)/g, whereas the calcined (900 °C, 6 h) sample shows 20.8 m\(^2\)/g and the reduction in surface area is attributed to growth in particle size with calcination.

### 3.4. Microstructural studies

The surface morphology of the grains of the sample was examined on a JEOL (JSM-840 A) scanning electron microscope (SEM). The SEM micrographs (Fig. 3) of combustion derived sample show that the powder products are voluminous and porous. As a result of high temperature (>1000 °C) during combustion process and partial sintering, agglomerated circular shaped primary crystallites were formed. The fluffy nature, voids in the combustion derived powders can be attributed to large amount of gases evolved during combustion reaction. Upon calcination of the sample, the size of primary particle increases which results in decrease in surface area of the sample as expected and it is confirmed by surface area measurements.

### 3.5. Infrared spectroscopy

IR spectra of as-formed and calcined (900 °C, 6 h) LBMO samples are shown in Fig. 4. The IR spectra of combustion derived manganites show two characteristic bands, one around 600 cm\(^{-1}\) corresponds to the stretching mode \( \nu_s \) of the Mn–O–Mn or Mn–O bond and another band around 400 cm\(^{-1}\) attributed to the bending mode \( \nu_b \). IR spectra show broad absorption peaks in the whole frequency regions, which may be due to
nanocrystallite size of the manganites [26]. In fact, the calcined powder (900 °C for 6 h) shows more defined and significantly less peak-broadening of the peaks due to particle growth. The growth of particles upon calcination is also manifested by scanning electron micrographs (Fig. 3), reduction in surface area (34–20.8 m²/g) and shifting of PXRD peaks towards lower angle (Fig. 1). The as-formed LBMO sample exhibits additional bands at ~670 and ~1380 cm⁻¹ which are assigned to BaCO₃ impurity [27]. However on calcination these bands disappear.

3.6. Magnetoresistance properties

Fig. 5(a) shows the temperature dependence of the resistivity of LBMO pellet (sintered at 900 °C for 6 h) at different magnetic fields. The TₓM-I of these samples are 228, 230, 231 and 232 K under 0, 1, 4 and 7 T, respectively. It can be seen from Fig. 5(a) that the resistance decreases with increasing magnetic field. This may be due to the fact that the applied magnetic field induces depression of charge carriers, which in turn might suppress the resistance and also causes the local ordering of the magnetic spins. Due to this ordering, the ferromagnetic metallic state may suppress the paramagnetic insulating regime. As a result, the conduction electrons (e₁g) are easily transferred between the pairs of Mn³⁺ (t₃₂g e₁g: S = 2) and Mn⁴⁺ (t₃₂g e₀g: S = 3/2) via oxygen [28]. In fact, application of a magnetic field will give the field-induced ferromagnetic ordering and hence reduces the resistance through whole temperature range we have investigated. At 1 T applied magnetic field LBMO shows MR of 10%, whereas for 4 and 7 T the negative magnetoresistance are in the range 51 and 60% respectively at 228 K. The magnitude of MR is defined as [ΔR/R(0)] = [R(H) − R(0)]/R(0), where R(H) and R(0) are the resistances at a given temperature in the presence and the absence of a magnetic field, H respectively. Fig. 5(b) shows temperature variation of MR of nanocrystalline LBMO sample at 1, 4 and 7 T. The %MR decreases monotonically with increasing temperature for all the applied fields. The presence of a sufficient concentration of ferromagnetic clusters seems to suffice for the observation of MR in LBMO sample. Magnetic clusters consisting of Mn³⁺/Mn⁴⁺ ions are responsible for double exchange mechanism: It explains both transport and magnetic properties of hole doped manganites. The parallel alignment of Mn-spin is required before hopping of electrons between Mn³⁺ and Mn⁴⁺ ions to give electrical conductivity. In the absence of magnetic field, the spins of Mn-ions may not be parallel, which makes the electron transfer between the pairs of Mn-ions is more difficult and resistance increases. When magnetic field is applied more number of spins of Mn ions get aligned and the transfer of electrons between Mn³⁺ and Mn⁴⁺ ions is easy and results in decrease in resistance.

In the low temperature regime (70–180 K), the electrical resistivity of divalent-doped LaMnO₃ is reported to be fit with an empirical equation [29,30] of the type

\[ ρ = ρ₁ + ρ₂T^n \]

where ρ₁ represents the resistivity due to grain boundary effect. The fitting to the equation yields a value of n = 2 with \( R^2 = 0.9971 \). The above fit shows the double exchange interaction plays a major role on the MR behavior of the sample.
The term $\rho_2 T^2$ indicates resistivity due to the electron–electron scattering process in ferromagnetic phase. The solid lines in Fig. 5(a) represent the fit. Further, the parameter $\rho_1$ in the presence of magnetic fields 1, 4 and 7 T, are found to decrease with the increasing magnetic field. The observed behavior may be due to the enlargement of magnetic domains with increasing magnetic field.

4. Conclusions

Nanophasic $\text{La}_{0.9}\text{Ba}_{0.1}\text{MnO}_{3+\delta}$ (LBMO) has been prepared by combustion route using corresponding metal nitrates as oxidizers and ODH as a fuel at much lower temperature. The synthesis temperature employed is lower than those currently used in conventional route and also the time taken for preparation is only few minutes. This method enables to the formation of homogeneous and good surface area nanocrystalline powders. We observed a metal–insulator transition temperature around 228 K. LBMO sample exhibit field-induced ferromagnetic orderings and shows negative magneto resistance. The resistivity data below $T_{M-I}$ could be fitted to double exchange model and shows double exchange interaction plays a major role in this compound.

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