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Low temperature synthesis, structural characterization, and zero-field resistivity of nanocrystalline $La_{1-x}Sr_xMnO_{3+\delta}$ ($0.0 \leq x \leq 0.3$) manganites

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Abstract

This paper reports the synthesis of nanocrystalline strontium doped manganites by a simple and instantaneous solution combustion method, which is a low temperature initiated route to prepare fine-grained oxide powders with good surface area. Rietveld refinement of X-ray data indicates that the as-formed manganites exhibit a cubic phase with space group *Pm3m*. However calcined (900 °C, 6 h) samples transform into rhombohedral phase with space group *R-3c*. The scanning electron micrographs of the powders reveal that the sizes of very fine primary particles which are in an agglomerated form, decrease as strontium content increases. The infrared spectra of lanthanum manganites show two active modes at 400 and 600 cm^{-1}. From zero-field resistivity measurements, it is found that all the samples exhibit metal–insulator transition (T_{M-I}) in the range of 219–252 K, which is low as compared to the samples prepared by ceramic route. The lower (T_{M-I}) values might be due to smaller particle sizes in the range of 25–45 nm.

Keywords: A. Magnetic materials; A. Oxides; B. Chemical synthesis; C. X-ray diffraction; D. Electrical properties

1. Introduction

The interesting physical and chemical properties of nanocrystalline materials have motivated the study of new synthetic routes to produce these special nanoparticles, which have new applications in the materials science and nanotechnology. It is well known that the processing conditions, microstructure, magnetic and transport properties of a material strongly depend on the crystallite size, because this could lower the phase transformation temperature and improve the sintering behavior of the material. It is of interest to investigate nanocrystalline samples with particle sizes comparable with magnetic domain sizes, in order to understand the mechanism for the colossal magnetoresistance (CMR) better. Combustion derived samples are polycrystalline materials. Because of grain boundary effect, polycrystalline manganites in nanodimension show a resistivity behavior differ from those reported in single crystals

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[1] and in samples prepared by the ceramic route [2]. Single crystals show sharp metal–insulator transition, whereas nanocrystalline manganites show broad metal–insulator transition. The sharp transition indicates the high homogeneity and high crystalline quality in single crystal. In fact nanosize manganites have a higher magnitude of the low-field magnetoresistance as compared to the samples obtained through high temperature ceramic route [3].

A remarkable property of manganites is the possibility of inducing ferromagnetism by cationic substitutions on the different sites of the antiferromagnetic (AFM) parent compound $LaMnO_3$ [4]. The hole doped Mn-perovskite oxides; such as strontium doped manganites are prime examples of a solid with a ferromagnetic conducting state caused by the double exchange mechanism. In this, there is exchange of electrons from neighboring Mn^{3+} ($t_{2g}^3e_g^1$) to Mn^{4+} ($t_{2g}^3e_g^0$) ions through oxygen when their core spins are parallel and hopping is not favored when they are anti-parallel. The localized spins of the t_{2g} electrons are coupled ferromagnetically by the doped holes in the partially filled e_g band introduced by the strontium atoms. Thus, the partially filled e_g band is responsible simultaneously for ferromagnetism (FM) and conduction in these manganites [5–8]. Among the doped perovskite manganites, $La_{1-x}Sr_xMnO_{3+\delta}$ is of interest due to its unique properties such as catalysis [9–11] and giant magnetoresistance [12,13]. It is also used as an electrode material for solid oxide fuel cells [14] due to its relatively good electrical conductivity, stability towards the electrolyte and catalytic activity for oxygen reduction. In continuation of our investigation on porous nanocrystalline/nanostructural materials [15,16] we explore the possibility of using the novel combustion process for the preparation of alkaline earth doped lanthanum manganites. Strontium doped manganites have been mainly synthesized by solid-state reaction route [17] which requires very high temperature, repeated grinding and sintering. For these reasons, alternative low temperature processing techniques [18–23] have been developed in solid-state chemistry.

In the present work, we report the preparation of $La_{1-x}Sr_xMnO_{3+\delta}$ ($0.0 \leq x \leq 0.3$) manganites through solution combustion route using oxalyl dihydrazide (ODH) as a fuel and the corresponding metal nitrates as oxidizers. The combustion technique has drawn considerable attention in recent years due to its unique combination of technologically relevant characteristics. This method, in fact, makes possible the rapid synthesis of several refractory inorganic materials and advanced ceramics [16,24], without the prolonged high temperature treatment of sintering. Solution combustion process is fast, requiring the least external energy input, the reactants are mixed in atomic/molecular level, so that the final product is obviously more homogeneous, nanocrystalline and has a larger surface area than those prepared by conventional solid-state method [25]. Phase purity and homogeneity are achieved at low temperature as low as 300 °C as against 1300 °C needed to synthesize these manganites using solid-state method. The combustion derived $La_{1-x}Sr_xMnO_{3+\delta}$ ($0.0 \leq x \leq 0.3$) samples have high Mn^{4+} content, so they exhibit cubic and rhombohedral phase and these phases are favorable for ferromagnetic and metal–insulator property in manganites. For instance combustion derived $LaMnO_3$ contain 34% (cubic phase) and 28% (rhombohedral) Mn^{4+} content in as-formed and calcined samples, respectively, and exhibit metal–insulator transition ($T_{M–I}$ value 222 K) behavior property, which is absent in the sample prepared by high temperature route.

2. Experimental

2.1. Synthesis of $La_{1-x}Sr_xMnO_{3+\delta}$

In the preparation of $La_{1-x}Sr_xMnO_{3+\delta}$, lanthanum nitrate $La(NO_3)_3{\cdot}6H_2O$, strontium nitrate $Sr(NO_3)_2{\cdot}4H_2O$ and manganese nitrate $Mn(NO_3)_2{\cdot}4H_2O$ were used as oxidizers and oxalyl hydrazine, $C_2H_6N_4O_2$ (ODH) as a fuel. ODH serves two purposes; (i) It forms complexes with the metal ions and facilitating homogeneous mixing of the cations in solution and (ii) is a source of carbon and hydrogen, whose combustion liberates heat and gaseous products (CO_2, H_2O, N_2, etc.). ODH was prepared in our laboratory using diethyl oxalate and hydrazine hydrate as reported in literature [26]. An aqueous solution containing metal nitrates and fuel (ODH) are taken in a petri dish of approximately 300 ml capacity. The excess water is allowed to evaporate by heating on a hot plate until wet powder is left out and then the petri dish is introduced into a muffle furnace maintained at 300 ± 10 °C. The reaction mixture undergoes thermal dehydration, ignites at one spot, with liberation of gaseous products and producing a voluminous combustion product. The stoichiometry of the redox mixture for combustion is calculated on the total oxidizing and reducing valencies of the oxidizers and the fuel, using the concepts of propellant chemistry [27]. Fig. 1 shows the flow chart for the manganites prepared by solution combustion method.

The structural characterization of weakly agglomerated porous nanocrystalline manganites were carried out by various techniques. The phase purity and crystal structure were examined by powder X-ray diffraction (PXRD) on