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Low temperature nucleation of Griffiths Phase in Co doped $LaMnO_3$ nanostructures

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ABSTRACT

We have reported magnetic properties of $La_{1-x}Co_xMnO_3$ nanostructures synthesized by hydrothermal route. The crystal structure has been characterized by X-ray diffraction (XRD) technique, which shows rhombohedral perovskite structure at room temperature. Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS) have been used to analyse morphology and chemical composition of prepared nanoparticles. Magnetic hysteresis loops of all the samples exhibit ferromagnetic behaviour at 10 K. Inverse susceptibility graphs as a function of temperature represent deviation from Curie Weiss law. The indication for short range ferromagnetic clusters well above Curie temperature is observed due to the Griffiths Phase (GP). It is proposed that the presence of GP arises from induced size effects of La and Co ions.

1. Introduction

The general structural formula for perovskite structure is ABO_3, where A can be alkaline or rare-earth element and B ions mostly come from transition metal cations. In this structure, coordination of A and B sites with oxygen anions is 12 fold and 6 fold, respectively [1]. Lowest limit of cationic radii at A and B sites are $r_A > 0.09$ nm and $r_B > 0.051$ nm, where A is larger cation and it is placed on edge of structure however B is smaller one and located in the centre [1].

Lanthanum manganite $LaMnO_3$ (LMO) has attracted extensive attention for its superior properties. Mixed valence lanthanum perovskites have been used in the read heads, data storage media and magnetic sensors. Various properties can be improved for enhanced room temperature applications and functionalities with some additional doping of other elements. Size-dependent properties in lanthanum manganites have been recently studied and a significant variation is observed in its various parameters [2,3]. Any significant change produced in the crystal lattice is well reflected in the variation of size of ionic radii and type of dopant [4]. Nano-scaled variations due to different dopants having various ionic sizes are subjected to a considerable change in the usability of lanthanum manganites [5].

It is well known that un-doped LMO shows ferromagnetic nature. But when lanthanum is substituted with divalent or trivalent cation such as Ca, Sr, Pb or Co etc. then mixed valence state of Mn appears. Due to the presence of mixed oxidation states (Mn^{3+}, Mn^{4+}) rapid hopping of electron between two states continues, which transform ground state into ferromagnetic also then manganate exhibits significant magnetic and electric properties. This double exchange of electron depends on the Mn-O bond lengths and Mn-O-Mn bond angle [6,7]. The physical properties and oxygen vacancies of these manganate perovskite type materials can be controlled by substitution of different metal cations at A and B sites [8,9]. In literature, structural, transport and magnetic properties of these materials have been tailored by doping with other cations [10–12].

Recently, perovskite manganates $La_{1-x}A_xMnO_3$ (A = Cu, Ba, Sr, Eu, Pr) have gained scientist's interest due to the existence of intriguing physical response like electronic ordering, large thermoelectric effect antiferromagnetic-ferromagnetic, ferromagnetic-spin glass and metal-insulator transitions [13–17]. The parent $LaMnO_3$ has a weak magnetic ground state with Jahn-Teller ions (Mn^{3+}) on octahedral lattice sites. Upon cooling, paramagnetic state gradually transfers to ferromagnetic at particular Curie temperature. The partial substitution of La^{3+} ions with rare earth elements

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or transition metals strongly affects the transport and magnetic properties of this system because of the production of holes into the lattice, creating Mn^{4+} ions and thus structure changes because of the difference in ionic radii of the substituents. Quenched disorder and phase inhomogeneity in manganites have gained considerable attention in scientific community. Such inhomogeneity includes preformation of ferromagnetic or metallic clusters above long range Curie temperature of ferromagnet in paramagnetic state. The region where materials are characterized by the existence of ferromagnetic clusters within paramagnetic state is referred as Griffiths Phase (GP) [18]. The GP was initially predicted for diluted Ising ferromagnets. In addition, this inhomogeneity is commonly observed in La site substituted compounds. In such compounds, ferromagnetism (produced because of double exchange interactions) and GP (due to quenched disorder and inhomogeneity) is introduced by La site substitution with divalent or trivalent cations. However, Mn site substitution by rare earth or transition ions have also been reported but the occurrence of GP is rare in such compounds [19]. Besides this, it has also been reported in numerous studies that O vacancies can play dominant role for the creation of GP [20,21].

In this study, the nanoparticles of multicomponent $La_{1-x}Co_xMnO_3$ ($0 \leq x < 1$) are firstly synthesized by hydrothermal method and then structural, morphological and detailed magnetic properties are studied systematically. The main goal of this study is to elucidate the magnetic properties of synthesized nanoparticles, which are explained with the help of room temperature and low temperature magnetic hysteresis loops, temperature dependent magnetization curves and modelling of Curie Weiss law and Griffiths phase.

2. Experimental details

2.1. Materials

In typical preparation of perovskite type oxides, the precursor solution was obtained by dissolving salts of selected metals, lanthanum nitrate ($La(NO_3)_3{\cdot}6H_2O$); cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$); manganese nitrate ($Mn(NO_3)_2{\cdot}4H_2O$), potassium hydroxide (KOH), and potassium permanganate ($KMnO_4$) in de ionized water. Herein, it is worth mentioning that all the chemicals were analytical grades and used without any further treatment.

2.2. Synthesis of nanoparticles

Cobalt doped perovskite nanostructures with general chemical formula $La_{1-x}Co_xMnO_3$ ($0 \leq x < 1$) with an interval of 0.2, were prepared by hydrothermal method. In typical synthesis of nanoparticles, solution of each metal was prepared by dissolving in 25 mL volume of de ionized water under constant stirring. The resulting solution was then mixed with aqueous solution of KOH to make it strongly alkaline. The subsequent mixture was then loaded into a 100 mL hydrothermal cell. The reaction was carried out by heating the cell at 220 °C for 12 h. After that, hydrothermal cell was cooled to room temperature, the supernatant liquid was discarded and remaining product was washed several times first with water and then ethanol. The final product was then centrifuged and dried in oven at 120 °C. The acquired product was grinded into fine powder and calcined at 850 °C for 5 h in a box furnace.

2.3. Characterizations

To investigate crystal structure of prepared samples, powder X-ray diffraction (XRD) patterns were recorded by (Rigaku D/Max-2400) operated at 40 KV and 200 mA using CuKα radiation source with Ni filter. The obtained patterns were then compared with standard JCPDS files for phase identification. The morphology and elemental composition of samples were possessed by field emission scanning electron microscope (FE-SEM: HITACHI S-4800) and energy dispersive X-ray spectroscopy (EDX), respectively. Room temperature and low temperature magnetic behaviour of prepared nanoparticles were determined by physical property measurement system (PPMS: Quantum Design, 9T).

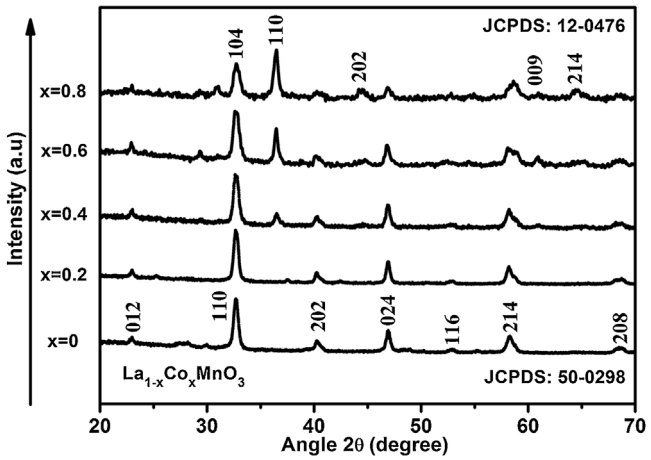

Fig. 1. X-ray diffraction (XRD) patterns of $La_{1-x}Co_xMnO_3$ perovskite nanoparticles at different compositions.

3. Results and discussions

3.1. Phase identification

To understand phase purity and crystal structure of synthesized samples XRD studies were carried out. Fig. 1 shows XRD patterns of $La_{1-x}Co_xMnO_3$ (x = 0, 0.2, 0.4, 0.6, and 0.8) after calcination of perovskite nanoparticles at 850 °C for 6 h in a box furnace. The patterns are indexed as rhombohedral perovskite structure with *R*3*c* space group. All perovskites are found to be well crystalline with perovskite phase without any noticeable extraneous phases. The main diffraction peaks appearing at 2θ = 23.02°, 32.47°, 32.77°, 40.25°, 46.86°, 52.68°, 58.23° and 68.59° correspond to (012), (110), (104), (202), (024), (116), (214) and (208) diffraction planes of phase pure perovskite structure, respectively. The obtained patterns are well-indexed with standard JCPDS file 50-0298 at $x \leq 0.2$. However, at higher doping concentration ($x \geq 0.4$) it has been observed that some intermediate phases appear due to the formation of $CoMnO_3$ and the observed peaks well match with the standard JCPDS file no: 12-0476 for $CoMnO_3$. In addition, large intensity peaks of doped $La_{1-x}Co_xMnO_3$ shift towards higher angle. This shift in peak can be associated to the strain and deformation produced in the crystal structure by cobalt doping at lanthanum sites, these factors can change lattice plane spacing and structural parameters. To determine crystallite size of particles Scherer analysis was performed on the most intense diffraction peak, using following formula [22];

$$D = \frac{0.9\lambda}{\beta cos\theta} \quad (1)$$

where, λ is wavelength of radiation used, β is full width at half maxima (FWHM) of the peak under consideration. In XRD pattern, it can be seen that with increase in doping concentration peaks become broad, which resultantly reduce the crystallite size of the nanoparticles. The calculated values of crystallite sizes with different dopant concentration of Co lie in the range of 17–13 nm and are given in Table 1.