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Structure and properties of electron-doped $Ca_{1-x}Sm_xMnO_3$ nanoparticles

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ABSTRACT

In this paper, we report the structural and magnetic properties of electron-doped $Ca_{1-x}Sm_xMnO_3$ (CSM) nanoparticles. The samarium's composition "x" was varied from 0 to 0.2 with the special attention up to 0.05. Spherical 60–70 nm polycrystalline CSM nanoparticles were synthesised by chemical co-precipitation technique. Doping of Sm^{3+} in antiferromagnetic $CaMnO_3$ has drastically altered its magnetic behavior due to the formation of ferromagnetic clusters. For example, the CSM powder with $x = 0.04$ displays about 115 K magnetic Curie temperature and about 0.1 emu/mole saturation magnetization. Physical properties of our nano-CSM powders are also compared with identical bulk-samples. To understand the differences, we invoked the intra-grain and inter-grain magnetic coupling process that facilitates to enhance their ferromagnetic behaviors. Unlike the bulk samples, such magnetic couplings in nanoparticles are favored by the presence of low-level crystal and interfacial defects.

1. Introduction

Doped perovskite manganites, chemical formula $RE_xCa_{1-x}MnO_3$ (where RE-rare earth elements), exhibit the various complex physical properties, such as colossal magneto-resistance (CMR), charge ordering (CO), orbital ordering (OO), ferromagnetism, and phase separations [1–3]. Consequently, the extensive studies were carried out on their structural and physical properties owing to the possibility of designing novel spintronic devices [1–3]. Such studies have undoubtedly shown that the doping of rare earth cations on Ca-sites provide the unprecedented control over their functional properties [1–6]. Recently, electron-doped manganites have also been studied as potential thermoelectric oxides because of their high-temperature chemical stability, unparalleled control over their electrical and thermal conductivity [6,7].

Doped-manganites are well studied in form of thin films, bulks, and single crystals [1–8]. However, these studies were usually focused in the 0.2–0.6 doping ranges wherein they display either CMR or CO/OO effects. Irrespective of the doping compositions, it is now a well-accepted fact that the unconventional properties in doped manganites originate because of simultaneous intricate interactions among their electronic, magnetic, and phonon order parameters. The typical characteristic length of these complex interactions varies from a few nanometers to micrometers [1–5]. Thus, the shrinkage in physical dimension of manganites below the characteristics lengths of various interacting order parameters will significantly affect their functional properties due to finite size and quantum effect.

In this context, few researchers have recently studied the nanoparticle behavior of manganites [8–12]. These studies clearly demonstrate that their properties have significantly altered by synthesizing them in nano-forms [8]. However, most of these studies were limited to the fixed doping composition with varying grain sizes [8–12]. They show that manganite-nanoparticles having 30 nm in sizes or below display superparamagnetic behaviours while above 100 nm, they display bulk like properties [8–18]. However, it is not yet clearly established that how doping of rare earth cation affects the electronic and magnetic properties of manganite nanoparticles, and further how their properties differ from ally bulk-samples. These factors have motivated our current study. Uniform CSM nanoparticles comprised of low level of crystal defects were synthesized and characterized by variety of techniques for their structural, transport, and magnetic properties. In order to avoid the complexity arising from superparamagnetic behaviours, we focused our studies on 60–70 nm CSM nanoparticles. We have also compared our results with published literature on related bulk samples and differences are elucidated.

2. Experimental details

Synthesis of nanosized CSM powders were carried out by co-precipitation technique which is advantageous in high productivity, better reproducibility, low cost, and homogeneity over large area of the samples. Calcium carbonate ($CaCO_3$, 99.99% pure), manganese carbonate ($MnCO_3$, 99.9%) and samarium nitrate

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($Sm(NO_3)_3{\cdot}6H_2O$, 99.99%) were first dissolved in dilute nitric acid with hydrogen peroxide as a promoter. Followed by it, distilled water was added to make it into nitrate stock solution. Ammonium carbonate was dissolved in distilled water, which would serve as the precipitant solution. The co-precipitation commenced by adding the nitrate stock solution into the precipitant solution, with continuous stirring for 2 h. The resultant suspensions were subjected to suction filtration. Subsequently, it was washed in water for four times and then allowed to dry at 100 °C. The dried material was calcined in the range of 600–800 °C for 6 h in air.

Crystallinity and structure of our samples were studied using the Bragg Brentano PW1850 Philips X-Ray powder diffractometer. The XRD patterns were collected in classical θ–2θ mode for 2θ varying from 10° to 90° using Cu Kα radiation source. Morphology of as synthesized powders was investigated by using a ZEISS supra 55 scanning electron microscope (SEM). Samples for transmission electron microscopy (TEM) studies were prepared by crushing the powder samples in butanol. Resultant flakes in suspension were deposited onto a holey carbon-coated copper grid. The Electron diffraction (ED) investigation was carried out with a 2010 JEOL electron microscope. On both microscopes energy dispersive spectroscopy (Si/Li detectors) allowed us to confirm that the chemical formulas of observed crystallites were in good agreement with expected nominal composition of our samples.

3. Results and discussion

3.1. Crystallinity and morphology

The development of crystallinity and phase formations of CSM nano-powders were examined by the XRD, SEM and TEM.

3.1.1. X-ray powder diffraction

In past, the crystal structure of CSM has been well studied. It exhibits orthorhombic *Pnma* symmetry [1–5]. A typical XRD pattern of $Ca_{0.96}Sm_{0.04}MnO_3$ powder calcined at 800 °C is shown in Fig. 1a. It shows that the powders are characterized by the sharp XRD reflections attesting that they are polycrystalline in nature. Further, it also shows that samples are free from impurity phases. Comparative XRD studies show that the powders processed at lower temperature display weak XRD reflections revealing their poor crystallinity. Further, they also contain peaks corresponding to the impurity phases. On contrast, a progressive increase in the processing temperature results into a drastic enhancement in their relative intensity of various XRD reflections. This clearly manifests that the crystallinity of our samples had been drastically improved. Further, the minor XRD peaks resulting from impurity phases were also disappeared. It inevitable demonstrates that the single phase CSM is formed. A further increase in the calcinations temperature resulted to obtain the well controlled, single phase, polycrystalline CSM powders. The detailed studies show that the crystalline phase was developed above 700 °C, and a single phase formed at around 800 °C (Fig. 1a).

Using XRD data, we extracted the lattice parameters of our samples. The estimated lattice parameters of $Ca_{0.96}Sm_{0.04}MnO_3$ were $a = 5.286(6)$ Å, $b = 5.272(5)$ Å and $c = 7.480(8)$ Å. The comparative detailed studies show that with a progressive increase in samarium's compositions, lattice parameters (Fig. 1b) of CSM increase monotonically and approaches plateau above $x = 0.1$. A similar trend was also observed in their unit cell volume. This enhancement in crystal parameters can be understood based on the difference in ionic radius of Sm^{3+} and Ca^{2+} [1–5]. The average grain size (t) of samples was also extracted from their corresponding XRD patterns using the Scherrer's formula. According to it, the average grain size $t = 0.9\lambda/B\cos\theta_B$, where λ is wavelength of Cu Kα radiation, θ_B is corresponding peak position and B is its full width at half maxima (FWHM) value. The estimated average grain size value was found to be in the range of 60–70 nm. Irrespective of the samarium's content, particle sizes of our all samples were the same.

3.1.2. Electron microscopy

To study further the microstructure and phase formations, electron microscopy studies were performed on these nano-powders.

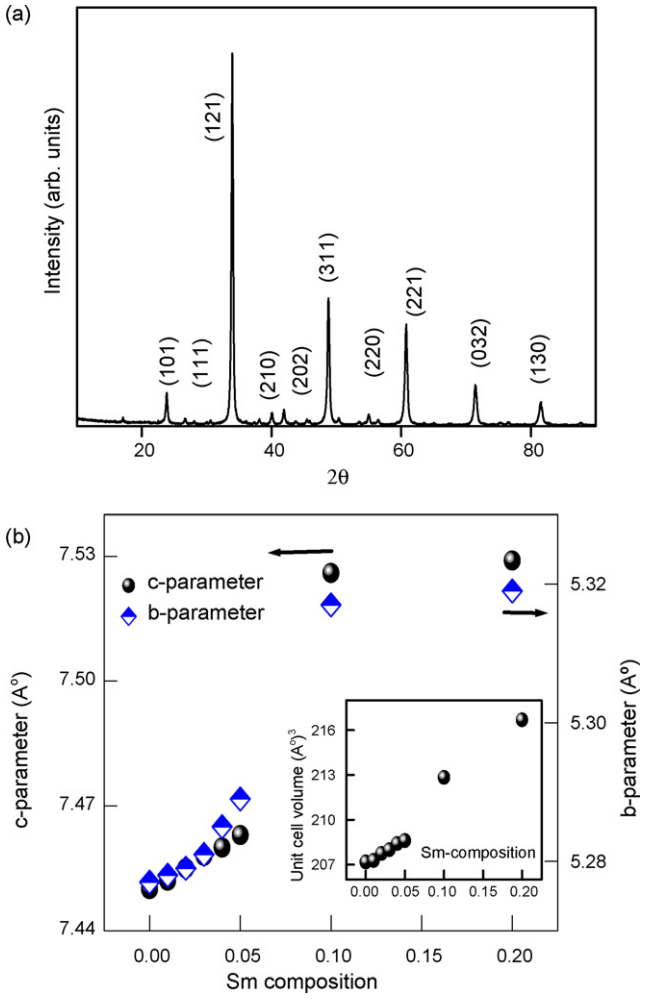

Fig. 1. (a) XRD pattern for a $Ca_{0.96}Sm_{0.04}MnO_3$ (CSM) sample calcined for 6 h at 800 °C and (b) variation in the lattice parameters and unit cell volume of CSM powder as function of samarium composition.

A typical SEM image of the as synthesized CSM powder is shown in Fig. 2. It clearly reveals that these powders are comprised of spherical aggregates of very small particles. Moreover, these aggregates are having uniform sizes (diameter around 2 μm). To study further its crystalline structure, TEM images (Fig. 3a) were recorded on a crushed sample. Fig. 3a shows the typical shape of nanoparticles. It shows that particles are characterized by the well-defined shapes

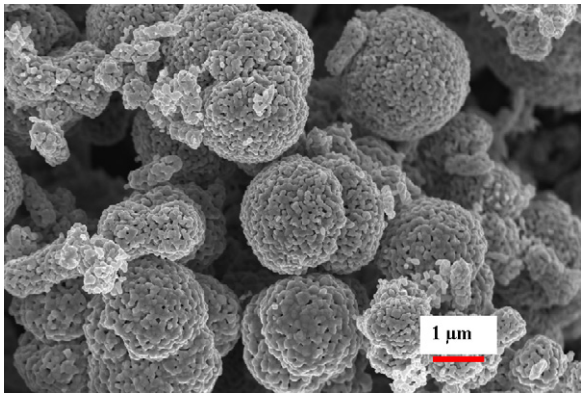

Fig. 2. A typical SEM image of as-synthesized CSM nano-powders. Morphology is characterized by the spherical aggregates. Small CSM particles are clearly evidenced.