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Synthesis and characterization of $LaMnO_{3+\delta}$ nanoparticles prepared by a simple thermal hydro-decomposition method

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This study reports the synthesis of $LaMnO_{3+\delta}$ (LMO) nanoparticles by a thermal hydro-decomposition method using acetate salts of La and Mn as starting materials. Thermal decomposition of the precursor was carried out at temperatures of 700, 800, 900 and 1000 °C for 6 h, to obtain the $LaMnO_{3+\delta}$ nanoparticles. The synthesized $LaMnO_{3+\delta}$ nanoparticles were characterized by XRD, FT-IR, SEM and TEM. Structural characterization showed that all the prepared samples had a perovskite structure, which changed from cubic to rhombohedral with increasing temperature of thermal decomposition. The crystallite sizes are in the range of 20 - 87 nm. Magnetic characteristics of the sample measured by a vibrating sample magnetrometer (VSM) at room temperature show paramagnetic behavior.

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1. Introduction

The perovskite manganites $A_{1-x}B_xMnO_{3+\delta}$, where A is a trivalent lanthanide cation (e.g, La) and B is a divalent cation (e.g., Ca, Sr, Ba and Pb) have recently attracted much attention because of their technical applications [1-3]. Among the others, the parent compound $LaMnO_{3+\delta}$ or LMO has been investigated thoroughly because it is of fundamental interest as a colossal magnetoresistive (CMR) material [2] and has been widely used in many applications including as electrode material for solid oxide fuel cells (SOFCs) [4], gas sensors, membranes for separation processes and catalysts etc. [5,6]. Traditionally, LMO is prepared by a conventional solid-state reaction at high temperature. This leads to a material with large particle size, poor compositional homogeneity and which requires a high sintering temperature for bulk fabrication. To date, a variety of chemical methods have been developed to prepare LMO nanoparticles at low cost and lower processing temperature, such as the citrate process [7], the polymeric precursor method [8], and hydrothermal synthesis [9], to name just a few. However among these established synthesis methods, it is still critical to find simple and cost effective routes to synthesize nanocrystalline LMO by using cheap, nontoxic and environmentally benign precursors.

In this paper, we report for the first time the synthesis of LMO nanoparticles by a direct thermal hydro-decomposition of metal acetate salts at 700 – 1000 °C. This synthesis route is very simple and cost effective. The prepared LMO samples were characterized by X-ray diffraction (XRD), Fourier Transform Infrared (FT-IR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The magnetic properties of the samples were also investigated by a vibrating sample magnetometer (VSM).

2. Experimental

In this study, the $LaMnO_{3+\delta}$ nanoparticles were prepared by a direct thermal hydro-decomposition method. In this process, high purity acetates of $La(CH_3COO)_3.xH_2O$ (99.9%, Aldrich) and $Mn(CH_3COO)_2.4H_2O$ (>99.9%, Fluka) were used as starting materials. In a typical procedure, 0.007 mol metal acetates with a mole ratio corresponding to the nominal composition of La : Mn ratio of 1 : 1 were dissolved in DI water. The ratio of DI water to the sum of acetate salts was 5 : 1 (v/wt.). Then, the mixed precursor was thermally decomposed in the oven under ambient atmosphere at various temperatures in the range of 600 – 1000 °C for 6 h. After grinding the thermally decomposed samples, LMO nanoparticles were obtained.

The crystal structure of the prepared samples of LMO nanoparticles was characterized by X-ray diffraction, XRD

(Philips PW3040, The Netherlands). The crystallite size of the samples was calculated from the half-width of a diffraction peak using Scherrer's equation [10]. The functional groups presented in the samples were studied by using Fourier Transform Infrared Spectroscopy, FT-IR (Spectrum One, Perkin Elmer Instrument, USA). The morphology of the samples was investigated by scanning electron microscopy, SEM (LEO 1450VP, UK) and transmission electron microscopy, TEM (JEOL 2010, 200 kV, Japan). The selected area electron diffraction (SAED) from TEM was analyzed to identify the phase and crystal structure to confirm the results obtained from XRD. The magnetic properties were investigated by a Vibrating Sample Magnetometer, VSM (Lakeshore VSM 7403, USA) at room temperature (20 °C).

3. Results and discussion

Fig. 1 shows the XRD results of the samples prepared at different temperatures for 6 h. All the samples show the main peaks of polycrystalline LMO except the sample prepared at 600 °C which shows the amorphous phase. The presence of an impurity phase of La_2O_3 (JCPD no. 050602) was observed in the samples thermally decomposed below 700 °C, while at above 700 °C an impurity phase of $La(OH)_3$ (JCPD no. 36-1481) was present. The crystal structure of the samples was clearly transformed from cubic to rhombohedral at above 900 °C and there are mixed phases of rhombohedral and cubic in the samples prepared above 800 °C. It is well known that no cubic phase was reported in the literature for $LaMnO_{3+\delta}$ [11]. Therefore, this structural transition may be due to non-stoichiometric effects such as cationic vacancy, Mn^{4+} content or Oxygen excess (δ) which may occur during the preparation process at above 800 °C, causing distortion of the crystal structure. The particle sizes of the prepared samples were determined by Scherrer's equation to be 20, 28, 62 and 87 nm for the samples thermally decomposed at 700, 800, 900 and 1000 °C, respectively.

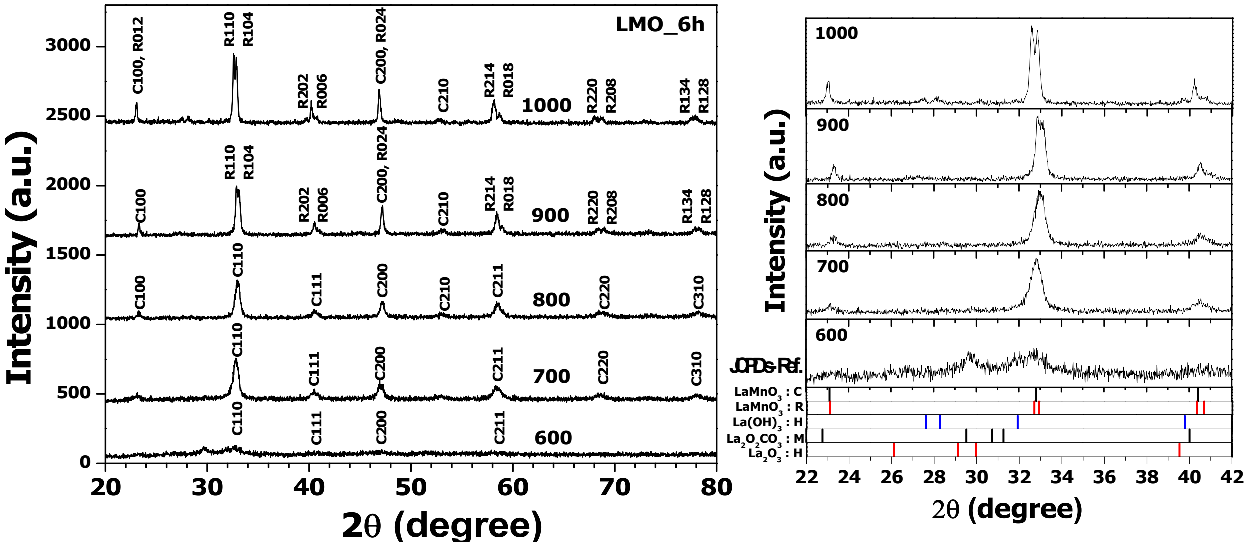

Fig. 1. XRD patterns of the $LaMnO_{3+\delta}$ nanoparticles prepared at 600, 700, 800, 900 and 1000°C for 6 h.

Fig. 2 shows the FTIR spectra of the standard, KBr, and the samples prepared at 600 -1000 °C for 6 h. Two absorption bands at around 600 cm^{-1} and 3600 cm^{-1} were observed in all the samples except the sample prepared at 600 °C which showed no absorption band at 600 cm^{-1}. The band at 600 cm^{-1} corresponds to the stretching mode, involving the internal motion of a change in the Mn-O-Mn bond length related to the environment surrounding the MnO_6 octahedra [12]. The absence of this absorption band for the sample thermally decomposed at 600 °C indicates that no perovskite phase of LMO was present in this sample. The bands at around 3600 cm^{-1} correspond to the $La(OH)_3$ peak which were found in samples prepared above 700 °C. These results are in good agreement with the XRD analysis (Fig. 1).

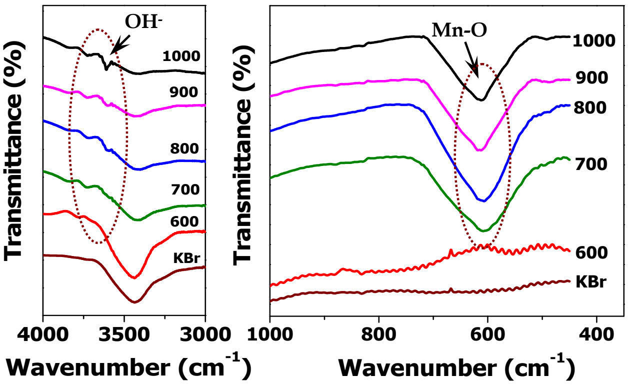

Fig. 2. FTIR spectra of the $LaMnO_{3+\delta}$ nanoparticles prepared at 600, 700, 800, 900 and 1000°C.

The morphology of the prepared samples revealed by SEM is presented in Fig.3. The SEM images show that the prepared samples consist of agglomerated spherical particles of 50-200 nm which are larger than the particle sizes obtained by Scherrer's equation from the XRD technique. This suggests that the agglomerated particles consist of very fine particles. It is clearly seen from Fig. 3 that the agglomerated particle size increases with increasing thermal decomposition temperature.

The detailed morphology and structure of the LMO sample prepared at 900 °C was further investigated by TEM and the result is shown in Fig. 4. From the TEM images (Fig. 4), the particle size of the sample prepared at 900 °C is about 90 nm which is in good agreement with the crystallite size of ~87 nm estimated from X-ray line broadening. The corresponding SAED pattern in Fig. 4 shows a spotty ring pattern suggesting a polycrystalline structure in the prepared sample. This result also confirms the mixed crystal structure of a major rhombohedral phase and a minor cubic phase in the sample prepared at 900 °C. This is in good agreement with the XRD results (Fig. 3). The insets of Fig. 4 show the high resolution TEM image (HRTEM) of the selected particle. The measured spacing of the lattice fringes is ~ 3.8880 Å, which corresponds to the interlayer spacing of the (100) plane of the cubic phase.

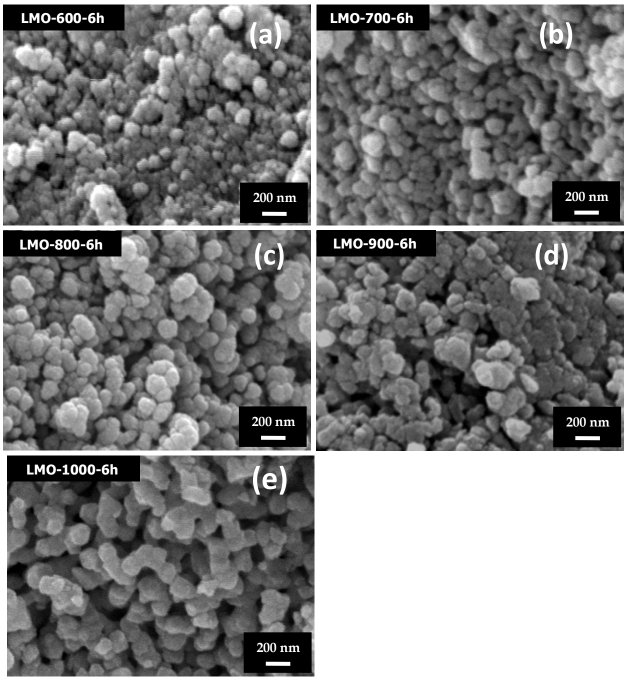

Fig. 3. SEM micrographs of the $LaMnO_{3+\delta}$ *nanoparticles thermally decomposed at (a) 600 °C, (b) 700 °C, (c) 800 °C (d) 900 °C and (e) 1000 °C for 6 h.*

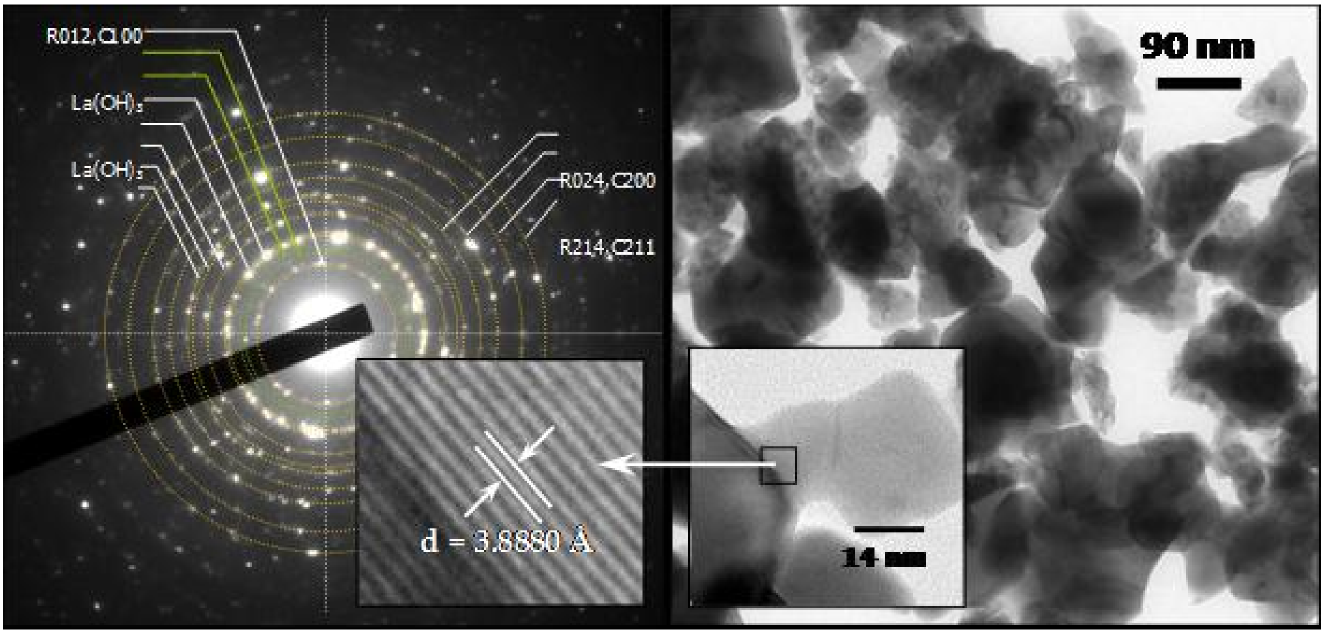

Fig. 4. TEM images with corresponding SAED patterns of the $LaMnO_{3+\delta}$ *nanoparticles thermally decomposed at 900 °C for 6 h.*

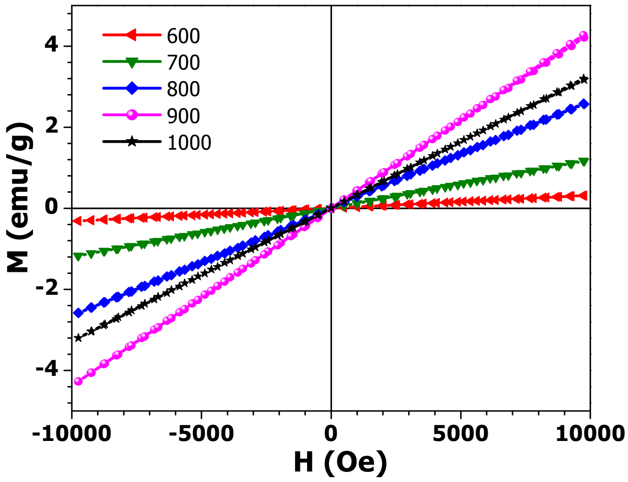

Fig. 5. Room temperature M vs. H of the LaMnO$_{3+\delta}$ nanoparticles thermally decomposed at 600, 700, 800, 900 and 1000 °C for 6 h.

Fig. 5 shows representative M-H curves of the prepared samples measured by VSM at room temperature. It is clearly seen that all the prepared samples exhibit paramagnetism because the Neel temperature (T_N) of LaMnO$_{3+\delta}$ is typically lower than room temperature (~140 K) [13]**.** The specific magnetization (M) increases with an increase in the thermal decomposition temperature. However, the decrease in M of the sample prepared at 1000 °C may be due to the impurity phase of diamagnetic La(OH)$_3$ present in the sample [14].

4. Conclusions

LaMnO$_{3+\delta}$ nanoparticles with particle sizes of ~20–87 nm have been synthesized by a simple thermal hydro-decomposition method. The structural characterization shows that the phase structure of the prepared particles changes from cubic to rhombohedral with increasing the temperature of thermal decomposition. The study of magnetic properties at room temperature shows that all the samples exhibit paramagnetic behavior. The present work proves that the hydro-thermal decomposition method is a new useful method for preparation of LaMnO$_{3+\delta}$ nanoparticles, and gives a potential avenue for further practical scale-up of the production process and applications.

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