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Sonochemical synthesis of $LaMnO_3$ nano-powder

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Abstract

We report the preparation of $LaMnO_3$ nanosized powder by the sonochemical process. Sodium dodecyl sulphate (SDS) was used as surfactant, to prevent agglomeration. The particle size obtained in this method was 19–55 nm. The phase formation temperature of $LaMnO_3$ was 700 °C which is lower than other conventional processes. So sonochemical process is cost effective and it is more acceptable considering its ease of preparation in comparison to other conventional processes. Powder synthesized was characterized by measuring crystallite size, specific surface area, morphology and by thermal analysis. The particle sizes of the powders were controlled by calcinations schedule. Narrow size distribution and core and shell structure of the prepared powder was revealed by transmission electron microscopy.

Keywords: Sonochemical; $LaMnO_3$; Nano-particle; TEM

1. Introduction

Recently lanthanum manganite have attracted a lot of attention for their application in cathode (solid oxide fuel cell) [1] and Giant magneto resistance materials [2].

Various methods have been tested to synthesize $LaMnO_3$ including the conventional solid state reaction [3], co-precipitation [4,5], sol–gel [6], molten salt reaction and hydrothermal synthesis [7]. In order to get homogeneous and nanosized lanthanum manganite powders, we applied sono-chemical method [8] as synthesis route.

Nano-structured materials offer novel properties like improved magnetization, quantum effects, and improved mechanical properties. By proper tuning of the particle size, it is possible to optimize the desired properties like electrical, magnetic, optical, thermal, mechanical, etc.

Sonochemical synthesis has been proven to be a useful technique to prepare nano-particles. The chemical effects of the ultrasound arise from acoustic cavitation, that is formation, growth, and implosive collapse of bubbles in a liquid [9]. There are two regions of sonochemical reactivity, the inside zone of the collapsing bubble and the interface between the bubble and the liquid. The cavitation can generate a temperature of around 5000 K and a pressure over 1800 kPa [10], which enable many chemical reactions to occur. In short, during the process, the implosive collapse of the bubbles generates localized hot spots through adiabatic compression or shock wave formation within the gas phase of the collapsing bubble. These extreme conditions attained during bubble collapse have been exploited to prepare various materials in different forms.

In our work, to synthesize nano-particle of $LaMnO_3$ we have used sonochemical technique using lanthanum nitrate and manganese acetate as starting materials. The formation temperature is 700 °C, which is lower than that of conventional processes. A suitable surfactant was added to get a comparatively high surface area of the powders. Sintered density of 97% of the powders can be achieved by the sonochemically prepared powders at lower temperature than that of conventionally prepared powders.

2. Experimental

0.1 M lanthanum nitrate and 0. 1 M manganese acetate aqueous solutions were taken in calculated quantity in a beaker. A small amount of decalin was added to the reactant mixture. Solvent like decalin, having low volatility are found to increase the power transfer to the system [11]. To reduce the agglomeration, 0.1 mmol/l SDS surfactant was added to the batch solution. Sonication was carried out by using direct immersion of Ti horn (20 kHz, 1500 W, Vibracell, USA) into the

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solution for 2 h at room temperature. Oxalic acid was added to the solution under sonication. The pH of the reaction mixture was 1. Sonication was continued for 4 h to ensure complete precipitation. The precipitate was collected and washed with alcohol and acetone. The powder was dried at 40 °C under vacuum. Finally the whole mass was calcined at a temperature range of 700–800 °C for 2–10 h. For conventionally prepared powder all the above-mentioned steps were performed, only sonication and related steps were omitted. For sintering studies, calcined powders were ground in a mortar in order to avoid any lump or grit. Then the powders were pressed uniaxially in form of pellet having diameter of 10 mm. Powders were very fine and no binder was added for pressing. Samples were sintered in a temperature range of 1000–1200 °C and a soaking time for 10–12 h. The densities of the samples were measured by Archimedes method using kerosene and a balance with a precision of $+10^{-4}$ g. The relative density, i.e., the ratio of the sample density to theoretical density was calculated.

X ray powder diffraction was performed on a X-ray diffractometer (Philips PW, 1710) using Cu Kα radiation λ = 1.5418 Å.

Thermo-gravimetric analysis and differential thermal analysis (DTA) were carried out on a Shimadzu thermal analyzer under air flow at a rate 10 °C/min. Differential scanning calorimetry (DSC) of the samples were carried out up to 500 °C (DSC 7 Perkin-Elmer). Specific surface area of the samples was estimated by N_2 adsorption–desorption method by applying BET equation. The instrument used was surface area analyzer (Micromeritrics, USA). The morphology and nano-structure of the powders were characterized by TEM (Jeol 230) using an accelerating voltage of 200 kV.

The percentage of Mn^{3+} and Mn^{4+} content in the samples were measured by iodometric titration method.

3. Results and discussions

XRD pattern presented in Fig. 1 shows a pure perovskite phase obtained after calcination at 700 °C. In contrast, in the earlier mentioned method phase pure compound could not be prepared at the above-mentioned temperature [12]. In this investigation, it is clear that by applying sonochemical process,

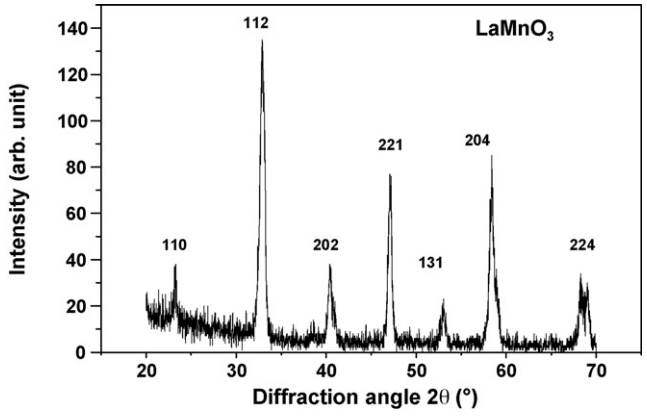

Fig. 1. XRD pattern of $LaMnO_3$ prepared by sonochemical method calcined at 700 °C.

Table 1
Change of crystallite sizes with temperature

Calcination condition		Mean particle size (nm)
Temperature (°C)	Time (h)	
700	2	19.0
700	6	32.0
700	10	53.0
800	2	25.0
800	6	55.0

lanthanum manganite can be obtained at lower temperature compared to other methods. The average crystallite sizes were measured by using Debye–Scherrer equation. The crystallite size calculated was 19–55 nm. The variation of particle size was controlled by calcinations temperature. The crystallite sizes of the powders are shown in Table 1. The powder prepared from sonochemical methods were thermally analyzed by TGA and DSC measurement. Fig. 2 shows the TGA curve of the reaction product of sonochemical synthesis. The total weight loss in the temperature range of 30–800 °C was 43%. The initial 5 wt.% loss up to ∼100 °C is due to the loss of adsorbed water and solvent. Next 9% loss ∼200 °C is attributed to removal of additives, i.e. decalin, SDS, etc., present in the powder. The 11% weight loss up to 340 °C, with a sharp rate attribute to decomposition of surfactant. And finally up to 600 °C, the 18% loss denotes the breaking of oxalate compounds and finally $LaMnO_3$ become stable.

Fig. 3a shows DSC of the prepared powders. Strong endothermic peak at ∼380 °C (650 K) represents the phase transition of $LaMnO_3$ (order–disorder transition). Latent heat related with phase transition was calculated from peak area. Here phase transition is related to the orbital order–disorder transition of $LaMnO_3$ nano-particles [13]. The variation of latent heat related with order–disorder transition, with particle size is shown in Fig. 3b. It is clear that latent heat rises by more than one order in magnitude up to 32 nm particle size, then drops sharply nearer to zero at a critical particle size 19 nm. This result shows that one can minimize the latent heat in $LaMnO_3$ around the orbital order–disorder transition point by

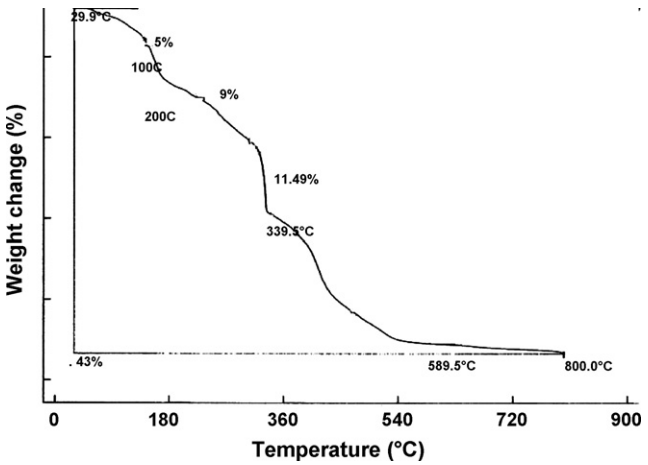

Fig. 2. TGA curve of $LaMnO_3$ powder.

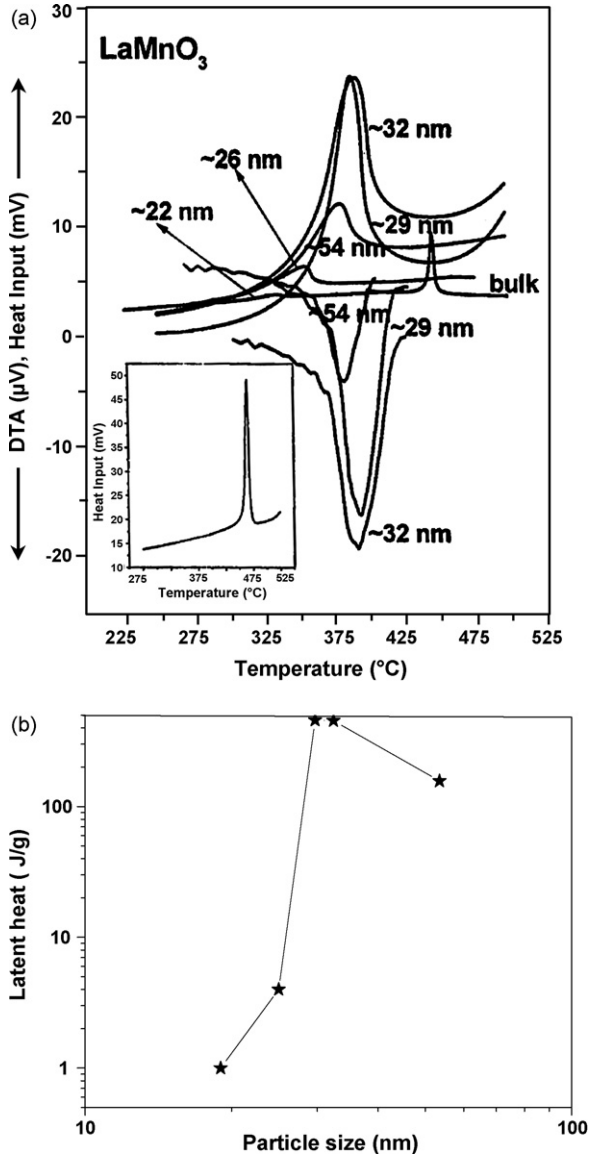

Fig. 3. (a) DSC pattern of $LaMnO_3$ powders. Inset pattern shows the DSC pattern of single crystal. (b) Variation of latent heat associated with orbital order–disorder transition with particle size.

restoring to nano-scale system. The Mn^{4+} concentration was measured by chemical analysis (redox titration) and is found to vary between 2 and 5 wt.%.

The specific surface area of the samples are in the range of 17–22 m^2/g. The surface area of the powders reduces drastically after calcination, which indicates the formation of agglomerates at that temperature. Relative density values of both powders, after sintering at equal condition are furnished in Table 2. Powders prepared by sonochemical process densified

Table 2
Change of relative density with sintering condition

Method of preparation	Sintering temperature		
	1000 °C/10 h	1150 °C/12 h	1200 °C/12 h
Conventional	89%	92%	94%
Sonochemical	90%	93%	97%

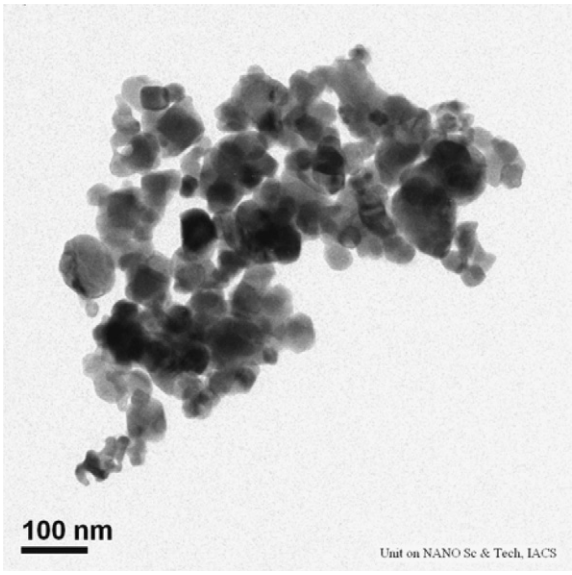

Fig. 4. TEM micrograph of $LaMnO_3$ powder prepared by sonochemical method.

at comparatively lower temperature than that of conventionally prepared powders. TEM images of the powders are shown in Fig. 4. Uniform sized particles are formed by sonication process. The uniformity of the size of the powders arise from uniform size distribution of bubble which acts as nano-reactor in case of sonochemical process. For nonvolatile precursor, the reactions occur in a 200 nm ring surrounding the collapsing bubble. The products are sometimes nano-amorphous, sometimes nano-crystalline in nature [14]. The size of the particles calculated from this TEM is almost same to that calculated from XRD peak broadening. The average particle size of the powders measured from TEM was 30 nm. Due to the agglomeration of the particles, it was not possible to measure enough particles to accurately report the particle size

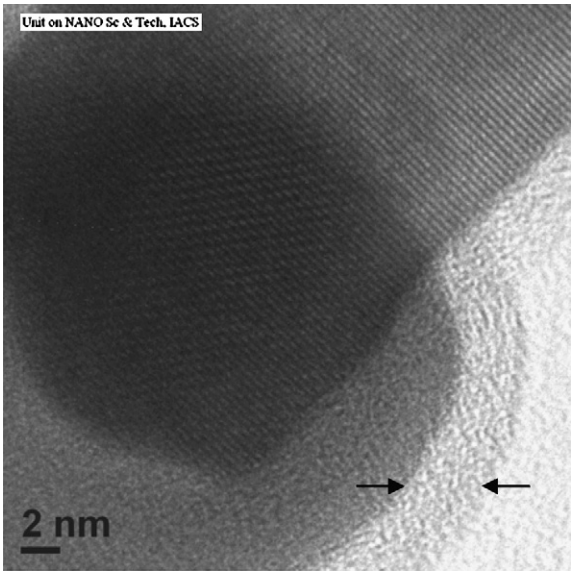

Fig. 5. Core–shell structure of individual particle (shell thickness is shown by arrow).

distribution of the powders. The reported particle size averages based on 21 particles. All these data are consistent and therefore, the qualities as well as the average particle size of the powders appear to be well defined.

Morphology of individual particle is shown in Fig. 5. Core–shell type particle morphology is to be seen. The inner core is crystalline and outer shell is amorphous in nature. The individual particle consists of 36 nm core and 6 nm shell. But as the width of the shell is very narrow SAED pattern from this region cannot be taken.

4. Summary

Currently, sonochemical technique has emerged as a cheap, simple and alternative route of fine powder preparation. It was demonstrated that sonochemical process can be used to prepare nanosized $LaMnO_3$ powders. The particle sizes of the powders were controlled by calcination conditions. Using sonication, a homogeneous reaction mixture is obtained. Homogenization ensures a lower formation temperature compared to other powder preparation methods.

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