Fabrication of Polycrystalline Lanthanum Manganite ($La_{0.99}Mn_{0.01}O_3$) Powder and Fibres by Electrospinning Method

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***Abstract*—Lanthanum manganite ($La_{0.99}Mn_{0.01}O_3$) powder have been prepared by using pyrolysis methods. Lanthanum manganite fibres were successfully fabricated by electro-spinning utilizing precursors. Polycrystalline perovskite structure lanthanum manganite powder and fibres showed that the grain size and crystal grain increased significantly with the increase in calcination temperature. A variety of techniques (SEM, FT-IR and TG-DTA) were employed to study the morphology and fibre quality, crystal structure, and thermal analysis of $La_{0.99}Mn_{0.01}O_3$ specimen respectively.**

***Keywords*— LanthanumManganite, Nanoparticles, perovskite, surface morphology, aqueous solution synthesis**

I. INTRODUCTION

$La_{0.99}Mn_{0.01}O_3$ powder has been prepared by using pyrolysis methods. The present work relates to as a material of various kinds of catalysts, electrodes and the like mainly in the form of a sintered body. A method for the preparation of a lanthanum manganite powder has problems in several respects. For example, it is almost unavoidable that a product obtained by calcinations and the amount of the unreacted starting materials can hardly be undetectably small even by conducting the process of calcinations at a higher temperature for a longer length of time than usually undertaken. [1-5]

When the lanthanum manganite is to be used in the form of a powder, in the application for thermal spraying and the like may faced in-convenience because growth of particles is unavoidable when blend to give a semi-sintered mass of coarse particles which must be disintegrated and finely pulverized. The product powder is poor in respect of the flowability behavior so that the powder is not suitable for use, for instance, in thermal spraying in which good flowability of the refractory powder is essential and in order not to cause briding of the powder in the feeder hopper.[6-10]

II. PREPARATION OF LANTHANUM MANGANITE ($La_{1-X}Mn_XO_3$, X = 0.01 mol) POWDER

First, we chose the compounds with reaction and studied about the Lanthanum (III) Chloride Heptahydrate ($LaCl_3.7H_2O$) and Manganese (II) Chloride Tetrahydrate ($MnCl_2.4H_2O$). The colour of $LaCl_3.7H_2O$ and $MnCl_2.4H_2O$ compounds are white-yellow and pink respectively. These specimen colour are paleness of crystals. $MnCl_2.4H_2O$ salt which occurs naturally as the rare mineral scacchite. The structure of $MnCl_2.4H_2O$ which consists of octahedral trans-$Mn(H_2O)_4Cl_2$ molecules. Also $LaCl_3.7H_2O$ is an excellent water soluble crystalline. These compounds were also studied with ammonium carbonate ($(NH_4)_2\ CO_3$). The $(NH_4)_2CO_3$ should be in the form of particles having an average particle diameter of at least 1μm or, preferably, from 10 to 100μm. $(NH_4)_2CO_3$ colour is white. When the particle size of the $(NH_4)_2CO_3$ particles is too small, no uniform aggregates of microcrystals can be obtained so as to badly affect the filterability of the composite carbonate precipitates with a decrease in the flowability of the $LaMnO_3$ powder prepared therefrom. The particle configuration of the ammonium carbonate particles is preferably spherical or cubic. Before starting aqueous solution, $LaCl_3.7H_2O$, $MnCl_2.4H_2O$ and $(NH_4)_2CO_3$ were weighted as 37.137 g, 19.790 g and 9.6 g, respectively. Each compound was obtained with mixing distilled water of 100 cc. The 0.99 mole of $LaCl_3.7H_2O$ and 0.01 mole of $MnCl_2.4H_2O$ were kept in a conical flask. This solution was stirred with magnetic stir on the gallenhamp stirrer machine about 10 minutes. During this time, $(NH_4)_2CO_3$ solution was added in the conical flask by using drop by drop method. The mixture solution in the flask was become precipitation for about 6 hours. The amount of $(NH_4)_2CO_3$ particles which were added to the aqueous solution is in the range from 1.5 to 3 times of the stoichiometric amount. As a result, white precipitate was appeared at ambient pressure under stirring. After doing the mixture for about 6 hours, the mixture was full of precipitation. By using the filter paper, the cream of compound was left on the paper. The cream of composite was then annealed at 100ºC for 30 minutes. The dry composite was then heated 2 times of 1000 ºC for 30 minutes each. Finally, the $(NH_4)_2CO_3$ particles was agitated at room temperature so that the carbonation reaction of the lanthanum and manganese compounds take place at or in the vicinity of the surface of the $(NH_4)_2CO_3$ particles to form precipitates of a composite carbonate of these elements. Thus, $LaMnO_3$ powder was obtained. Pure $LaMnO_3$ nano powder was taken by solution combustion method using metal chloride as oxidants. The morphology of $LaMnO_3$ nano powder was investigated by Scanning Electron Microscopy (SEM). Fourier Transform Infrared Radiation (FT-IR) was taken determination of the structure of crystalline materials such as; crystal axes, size and shape of the unit cell, positions of the atoms in the unit cell. $LaMnO_3$ powder was used by Thermo-

gravimetric (TGA) which is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. In this study, La_{1-x} Mn_xO_3 powder ferrites corresponding to the non-stoichiometry La_{1-x} Mn_xO_3 (x = 0.01, 1-x = 0.99) were synthesized from the inorganic agent and compared with respect to morphology, chemical composition and position in the unit cell, weight in relation to change with temperature and flowability.

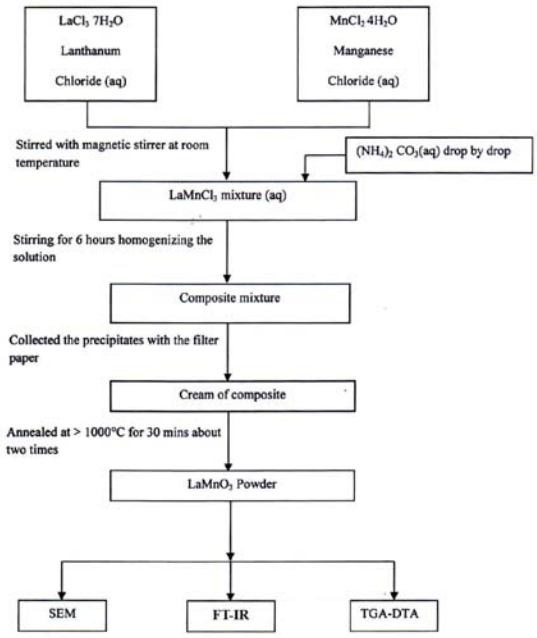

Fig.1(a) The block diagram of preparation of $LaMnO_3$ (x = 0.01 mol) Powder

Fig 1(b) Photo of the electrospinning experiment setup.

III. PREPARATION OF LANTHANUM MANGANITE $LA_{0.99}MN_{0.01}O_3$ FIBRES

First, inorganic agents were chosen for the preparation of the solution. Lanthanum manganite ($LaMnO_3$) and Poly Vinyl Alcohol (PVA) were consisted of 0.45g and 6g in the solution. To get Sol-gel aqueous solution, these compound were prepared by mixing with distill water of 50cc at room temperature. This aqueous solution was stirred to be homogenous until round about two hours. We got the gel-like solution after two hours. Viscosity results of $LaMnO_3$ sol-gel has been found 1400 and over at centi-point (c.p). The $LaMnO_3$ sol-gel could be done to spin in the Electrospinning machine. The $LaMnO_3$ gel-like solution was take in the syringe of 5mL. Before making spray; the glass-wall the vacuum tube was cleaned with alcohol. The aluminium (Al) foil was cut with glass-tube size (9cm) and it was put in the glass-vacuum tube. The level of vacuum was tested with the vacuum tester. The colour of violet was expressed no air in the glass tube. The electrospinning process took place in cylindrical shape of glass tube (36cm) that had very limited exposure to elements exterior to the tube. During spraying on the Al-foil, high voltage (29kV) was used from flight back for 3 minutes each until about for 20 minutes. The Al-foil with $LaMnO_3$ was taken in the vacuum of the tube for 30 minutes. Then, it was taken out from the vacuum tube and it was put in a box for 2 days at the atmosphere. The $LaMnO_3$ foil was annealed difference temperature at 500°C, 600°C and 700°C for 1 and half hours, 1 hour and 45 minutes respectively. After heating these foils, the surface morphology of the $LaMnO_3$ foils had been studied by SEM.

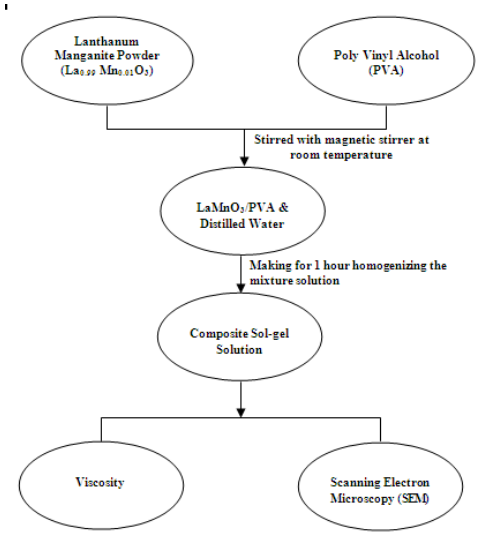

Fig. 1 (c) Word diagram of $LaMnO_3$ fibres

IV. RESULTS AND DISCUSSION

The surface morphology of $La_{0.99}Mn_{0.01}O_3$ has been studied by scanning electron microscopy (SEM). SEM is producing high resolution images of a sample surface. SEM images have a surface structure of the sample. SEM analysis was performed to examine the particle size and the micro and nano structural properties of $La_{0.99}Mn_{0.01}O_3$ powder and fibres phases. The observed SEM photograph was shown in Fig 2(a),

2(b), 2(c), 2(d), 2(e), 2(f), 2(g) and 2(h) for powder and Fig 3(a), 3(b), 3(c), 3(d), 3(e) and 3(f) for fibres.

Fig. 2(a) showed the fairly dense image with fine grain size at × 8.59k magnification and particles was used the working distance (WD) 6.5mm. The uniform grain distribution was seen on SEM image. The particle size was calculated to be 1µm. The grain-oriented was right side and SEM image was a little smooth. The resulting grain shape was found to be coral.

Fig. 2(b) constituted the highly dense image with fine grain size at × 6.69k magnification and its working distance (WD) 6.5mm. The homogeneous grain distribution was observed on SEM image. The calculation of the particle size was to be 2µm. The orientation of grain was right side and SEM image was smooth. The shape of resulting grain was seen to be like cloudy.

Fig. 2 (c) had the strongly dense image with good size of grain at × 6.69k magnification and its distance by working (WD) 6.5mm. The fairly homogeneous grain distribution was investigated on SEM image. The particle size was obtained to be 1µm by calculating. The direction of grain was right side and SEM image was fairly smooth. The shape of grain was resulted to be island.

Fig. 2(d) constituted the quite dense grain size at × 4.13k magnification with the working distance (WD) 6.5mm. The fine homogeneous grain was distribution on SEM image. The calculation of particle size was to be 2µm. The phase of grain was left side and SEM image was a little rough. The grain shape was observed to be like map.

Fig. 2(e) contained the magnification image size at × 21.65k and its working distance (WD) 7mm with a good dense. A well homogeneous grain was left - shifted on the image of SEM. The phase grain was calculated to be 200nm and its image was a little smooth. The grain shape was found to be cotton.

Fig. 2(f) included the magnified image size at × 14.28k within the working distance (WD) 7.5mm. The homogeneous grain was observed with the distribution of image on SEM. The particle size was calculated to be 1µm. The orientation of grain was right - shifted and its magnified image was rough. The shape of grain was seen to be like stone.

Fig. 2(g) involved the size of magnified image at × 18.33k within the working distance (WD) 7.5mm. The distribution of grain was modified with intense homogeneously. The particle size had to be 300nm by calculating. The phase of grain was formed to be the right side and well smooth. The shape of grain was performed to be like cotton.

Fig. 2(h) produced the size of magnification image at × 9.42k and its image working distance (WD) 7.5mm. The grain was performed with homogeneous. The particle size had calculated to be 1µm. The grain was formed to be right-orientation and smooth. The grain shape was examined to be like rock.

Fig. 3(a); according to SEM observation of $La_{0.99}Mn_{0.01}O_3$ sample can seen the composite on the Al-foil. This fibre composition was examined to be 300nm by calculating. The majority of the $La_{0.99}Mn_{0.01}O_3$ fibre composition was found to be right-orientated side and was clearly observed at 500ºC for 1 and half hour.

Fig.3(b); this fibre composition can seen 1µm of the sample calculation. The composite fibre was formed to be right side orientation at 500ºC for 1 and half hour.

Fig. 3(c), 3(d) and 3(e); the composite fibres had calculated to be 200nm, 200nm and 200nm but they had the difference magnification at × 19.25k, × 39.03k and × 25.75k and their working distance was made at 7.5mm, 7mm and 7mm. Only fig 3(e) showed the length of fibre and its phase was formed to be left-orientated side. The fibre distribution was clearly observed at 600ºC for 1 hour.

Fig. 3(f); the magnification of fibre composition was performed the size at × 5.26k and its working distance (WD) 7mm from the SEM image. The fibre composition size was calculated to be1µm and it was randomly showed its phase at 700 ºC for 45 minutes.

FT-IR technique can be used to study for the vibrational properties of molecules in materials, such as frequencies or wavelengths of the radiation and the amount of radiation absorbed by the sample. FT-IR offers quantitative and qualitative analysis for inorganic and organic samples. The resulting spectrum produces a profile of the sample, a distinctive screen and scan samples for an effective analytical instrument for detecting functional groups and characterizing covalent bonding information. Single fibres or particles are sufficient enough for Perkin-Elmer FT-Raman Spectrometre in this research work is shown in Fig.

IR transmission spectrum of $La_{0.99}Mn_{0.01}O_3$ powder within the wavenumber ranges of $500cm^{-1}$ - $4000cm^{-1}$ and $520cm^{-1}$ -$4000cm^{-1}$ region is shown in Fig 4(a) and 4(b). From the figure 4(a); there were eight Raman lines were collected within the Raman shift region of $520cm^{-1}$ - $4000cm^{-1}$ at 1000Ċ for 30 minutes. Their resolutions were found at $3480cm^{-1}$ for 14 minutes (840 seconds). The transmittance lines their wavenumbers were significantly obtained at 40%T, 63%T, 62%T, 74%, 79%T, 69%T, 73.5%T and 75%T and $513cm^{-1}$, $590cm^{-1}$, $625cm^{-1}$, $673cm^{-1}$, $704cm^{-1}$, $713cm^{-1}$, $1190cm^{-1}$ and $1375cm^{-1}$.

From the figure 4(b); Raman lines had the three shift region of $510cm^{-1}$-$1416cm^{-1}$ at 1000ºC for 30 minutes. The resolutions were showed at $906cm^{-1}$ for 12 minutes (720 seconds). Those transmittance and wavenumbers were collected at 73%T, 76%T and 97%T and $511cm^{-1}$, $628.79cm^{-1}$ and$1415cm^{-1}$, respectively.

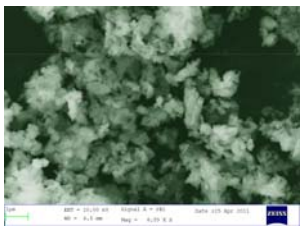

Figure 2 (a) SEM of $La_{1-x}Mn_xO_3$ (x = 0.01 mol) powder at 1000°C for 30 minutes

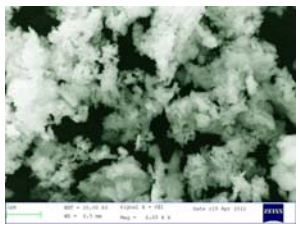

Figure 2(b) SEM of $La_{1-x}Mn_xO_3$ (x = 0.01 mol) powder at 1000°C f or 30 minutes

Figure 2. (c) SEM of $La_{1-x}Mn_xO_3$ (x = 0.01 mol) powder at 1000°C for 30 minutes

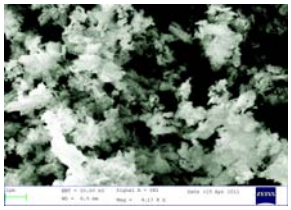

Figure 2. (d) SEM of $La_{1-x}Mn_xO_3$ (x = 0.01 mol) powder at 1000°C for 30 minutes

Figure 2. (e) SEM of $La_{1-x}Mn_xO_3$ (x = 0.01 mol) powder at 1000°C for 30 minutes

Figure 2. (f) SEM of $La_{1-x}Mn_xO_3$ (x = 0.01 mol) powder at 1000°C for 30 minutes

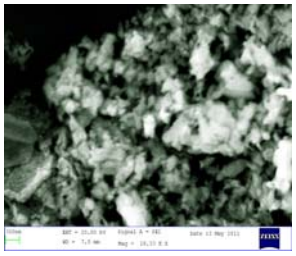

Figure 2. (g) SEM of $La_{1-x}Mn_xO_3$ (x = 0.01 mol) powder at 1000°C for 30 minutes

Figure 2. (h) SEM of $La_{1-x}Mn_xO_3$ (x = 0.01 mol) powder at 1000°C for 30 minutes

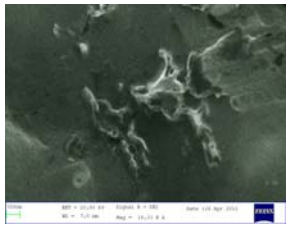

Figure 3. (a) SEM of $La_{1-x}Mn_xO_3$ (x = 0.01 mol) fibre at 500°C for 1 and half hours

Figure 3. (b) SEM of $La_{1-x}Mn_xO_3$ (x = 0.01 mol) fibre at 500°C for 1 and half hours

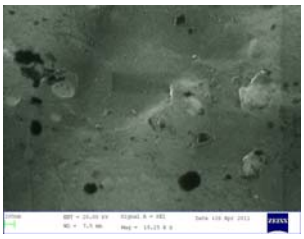

Figure 3. (c) SEM of $La_{1-x}Mn_xO_3$ (x = 0.01 mol) **fibre at 600°C for 1 hours**

Figure 3. (d) SEM of $La_{1-x}Mn_xO_3$ (x = 0.01 mol) fibre at 600°**C for 1 hours**

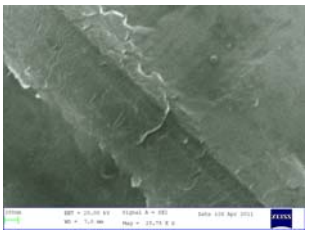

Figure 3. (e) SEM of $La_{1-x}Mn_xO_3$ (x = 0.01 mol) fibre at 600°C for 1 hours

Figure 3. (f) SEM of $La_{1-x}Mn_xO_3$ (x = 0.01 mol) fibre at 700°C for 45 minutes

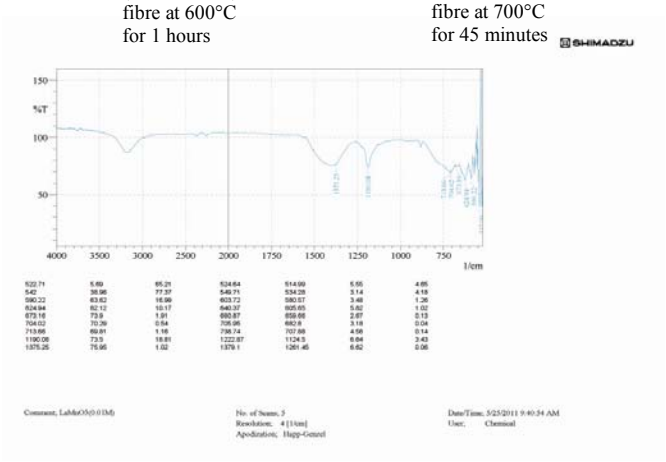

Figure 4. (a) IR transmission spectrum of $La_{1-x}Mn_xO_3$ (x = 0.01 mol) powder at 1000°C for 30 minutes within the wave number ranges of 520-4000 cm^{-1}

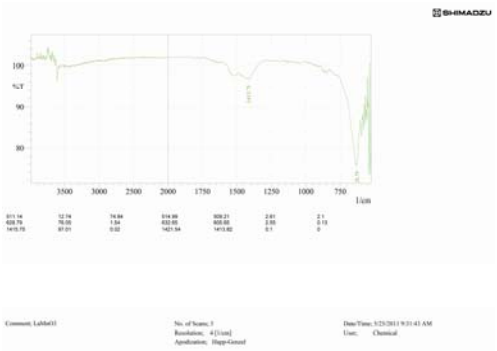

Figure 4. (b) IR transmission spectrum of $La_{1-x}Mn_xO_3$(x = 0.01 mol) powder at 1000°C for 30 minutes within the wave number ranges of 510-4000 cm^{-1}

Thermal Gravimetic Analysis (TGA) is a simple analytical technique that measures the weight loss or weight gain of a material as a function of temperature. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were shown in Fig.5 (a) and (b). This figure showed that the $LaMnO_3$ powder has no crystalline water and no phase transition before decomposition. Complex degradation of $LaMnO_3$ compound take place above 230ºC. The decomposition, point of $LaMnO_3$ powder was at 230ºC and 310ºC. Major weight lose occurs at 410°C.

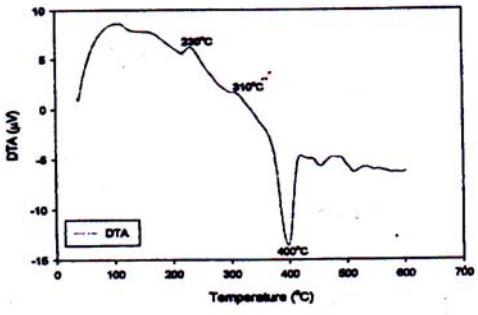

Fig.5(a) DTA thermograms of $LaMnO_3$ powder

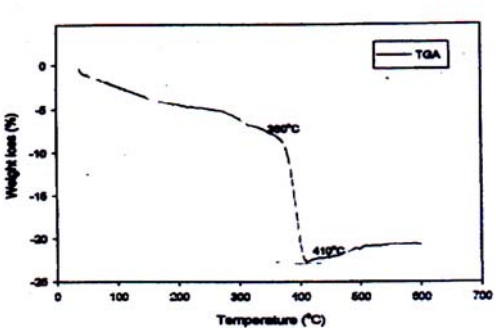

Fig. 5(b) TGA thermograms for weight loss of $LaMnO_3$ Powder

Growth and characterization of $La_{0.99}Mn_{0.01}O_3$ powder and fibre have been successfully investigated. According to the FT-IR results, $La_{0.99}Mn_{0.01}O_3$ powder was successfully formed at given temperature. Some unnecessary peaks were formed and unidentified. This might be attributed to the formation of some impurities during processing and secondary oxides.

From SEM imager, morphological change in $La_{0.99}Mn_{0.01}O_3$ powder was observed. From SEM image of $La_{0.99}Mn_{0.01}O_3$ fibre composition were calculated 1μm and 200nm. According to the TGA curve, $La_{0.99}Mn_{0.01}O_3$ was thermally stable and final weight loss was completed at about 400°C. The exothermic peak was formed at about 410°C on DTA curve. Thus the exothermic DTA peaks were associated with the TGA weight loss and were indicative at organic combustion steps. Therefore, the $La_{0.99}Mn_{0.01}O_3$ specimen was crystalline at about 400°C. The combined TGA and DTA data indicated that slow heating results in transformation of the colloidal solution (sol- gel like solution) to crystalline $La_{0.99}Mn_{0.01}O_3$ at about 400°C. The choice of starting chemical, growth mechanism is quite suitable for powder/ceramic growth technology.

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