Study on Lanthanum Manganite Ultra-fine Fibres

Zin Min Myat[1], Taw Taw[2], Sabai Aye[2], Than Than Win[2], Yin Maung Maung[2] and Ko Ko Kyaw Soe[2]

[1]Department of Physics, University of Dagon, Yangon, Myanmar
[2]Department of Physics, University of Yangon, Myanmar

Abstract-Local-made electrospinning experimental set-up is firstly constructed. Lanthanum Manganite ($La_{0.98}Mn_{0.02}O_3$) nano fibres are fabricated by electrospinning utilizing sol-gel precursors. The crystal structure and thermal analysis are studied by Scanning Electron Microscope (SEM), X-ray diffraction (XRD) and Thermogravimetry and simultaneous Differential Thermal Analysis (TG-DTA) respectively.

Keywords*: Lanthanum Manganite, XRD, SEM, TG-DTA*

I. INTRODUCTION

The science and technology of nanostructured materials is advancing at a very quickly pace. Nowadays the preparation and functionalization of one-dimentional nanostructured materials has become one of the most important role of the Nanotechnology. Nano fibres can be made of lanthanum manganite ($LaMnO_3$) by electrospinning technique. In order to obtain these fibres, $LaMnO_3$ powder is required and is proposed mainly from the lanthanum chloride, manganese chloride and ammonium carbonate used as the starting materials [1].

Nanoscales elemental powders and suspensions as alternative high surface area forms may be considered lanthanum chloride is the very important raw materials for FCC catalyst and water treatment. Manganese chloride $MnCl_2.4H_2O$ (aq) is a pink salt that occurs naturally as the rare mineral scacchite. [2, 3].Electrospinning is a technique for producing polymer fibres in the range 20 μm to 50nm by accelerating a charged polymer solution using a high electric field. Electrospinning is a unique approach using electrostatic forces to produce ultra-fine fibres. Nanofibres can be made of lanthanum manganite ($LaMnO_3$) by electrospinning technique [5].

The microstructure of the precipitates of the composite carbonates formed by mixing aqueous solutions is studied. The purpose of this paper is to grow and characterize the sample preparation and to investigate the crystallographic and morphological features of the $LaMnO_3$ nano powders in the temperature range 800°C- 1200°C and ultra-fine fibres in the temperature range 400°C - 800°C.

II. EXPERIMENTAL PROCEDURE

In the present investigation, lanthanum chloride ($LaCl_3$), Manganese chloride ($MnCl_2$) and ammonium carbonate $(NH_4)_2CO_3$ were used as starting materials. All chemicals were analytical grade and directly used as received without further modification. Distilled water was used as solvent. Lanthanum chloride, manganese chloride and ammonium carbonate in amounts of 37.137 g, 19.79 g and 50 g were weighted respectively and dissolved in 100 ml of distilled water. These solutions were mixed with different molar ratio to get this composition $La_{0.98}Mn_{0.02}O_3$ (abbreviation: LMO). Firstly, $LaCl_3.7H_2O$ and $MnCl_2.4H_2O$ solutions were mixed together and stirring with magnetic stirrer for six hours at room temperature.

During stirring, ammonium carbonate was poured drop by drop in the mixture solution until to get homogeneous and appropriate solution. When the aqueous solution was prepared by dissolving neutral salts of the respective elements in water, the solution prepared may have a pH level of 6 to 8 so that no further adjustment of the pH is required as a matter of course. The precipitates were collected by filtration to obtain the cream of lanthanum manganite composite mixture. The prepared composite cream was dried initially at 100°C for 2 h under vacuum, and then calcined at a heating rate of 2°C/min. Thus LMO powder was obtained when calcinations temperature was 1000 °C for 30 minutes. XRF and SEM were carried out to investigate the elemental composition and the microstructure of the derived sample respectively. TG-DTA analysis was carried out at a temperature rising rate of 100°C/min under stable air conditions. The crystallization quality, as well as out-of-plane and in-plane orientation was characterized by X-ray diffraction (XRD). Possible formation mechanism of LMO sample was characterized by XRF, TGA-DTA, SEM and XRD. A few steps during the preparation of LMO nanocrystalline materials were fabricated by calcinations of these composite and some new results were achieved.

The mixed solution was prepared by mixing amount of salts with doubly distilled water and was added 0.1 ml of NH_4OH. Then these solutions were stirred with glass rod for 30 min to disrupt gel structure. After stirring, the temporary solutions were mixed at room temperature for 24h to get a uniform solution. The obtained uniform solution was refluxed at 80°C for 4h. After being cooled, the clear solution was measured by capillary tube to know viscosity. This process of washing was repeated 5 times for each batch of precipitated gel. The washed solution was then refluxed on oven at 100°C for 30min and cooled down to room temperature. After being cooled, the sol-gel solution was combined with 0.1 ml of acetic acid to prevent gel structure. Finally, that solution was determined by measuring its viscosity. 0.54 g of $LaMnO_3$ was dissolved in 7 g of Poly vinyl Alcohol (PVA). The mixtures of

these were dissolved in distilled water. The mixture was stirred by magnetic stirrer for 3h to form a homogeneous solution. The solution was expected to be viscous enough for electrospinning. The precursor solution was taken in a syringe with hypodermic needle (0.55×25mm). The hypodermis syringe needle was connected to the positive terminal of a high DC voltage generator that produce maximum voltage 26.20 kV and the negative terminal of the power supply was connected to the collector (Aluminium foil) opposite to the syringe needle with a distance about 11cm. Al-substrate was then stuck on the collector. Before supplying the power, glass tube was created as vacuum condition by using vacuum pump and also tested by vacuum tester. The high electrical potential overcomes the surface tension of the solution in the syringe needle and the jet of charged precursor solution was ejected out from the needle to the collector. The precursor solution was deposited on Al substrate by electrospinning method. And then it was heat-treated at 800°C for 45 min. Possible formation mechanism of $LaMnO_3$ fibres was characterized by XRD. The morphology and size of the fibres were observed with Scanning Electron Micorscope (SEM).

III. RESULTS AND DISCUSSION

Lanthanum manganite powder was obtained by calcinations of the precipitates of the composite carbonate. In order to investigate the lowest crystallizing temperature and the variety of phases, the composite powder was characterized by X-ray fluorescence (XRF). The different concentrations should be clearly visible as shown in Fig 1. According to XRF graph, it was found that the concentration of La was (82.051%) and Mn was (3.461%). Fig 2 showed the SEM image of LMO powder sintered at 1000°C exhibit grained microstructure with small crystallite size. It should be assumed that it was spread uniformly on the surface areas. The powder was composed by spherical shaped densely packed particles. The calculation of the grain size was to be 0.32 μm. The orientation of grains was right and SEM image was a little rough. The resulting grain shape was seen to round cotton. The colour of the powder at 1000°C is white. The DTA of the $LaMnO_3$ of mixed carbonate showed four district endothermic peaks in Fig 3 (a). The first endothermic peak at 140°C may be due to the loss of moisture from the $LaMnO_3$ composite sample. The endothermic peak at 170 °C corresponds to the decomposition of $LaCO_3$ to La_2O_3 on the other hand; $MnCO_3$ decomposition takes place in three steps corresponding to the endothermic peaks at 170 °C, 260 °C and 400 °C which finally results in MnO_3 formation. It may be inferred that the endothermic peak around 400°C represented the decomposition of $LaCO_3$ as well as the initial stage of $MnCO_3$ decomposition. The endothermic peaks at 398.6°C and 543.34°C were indicative of subsequent stages of $MnCO_3$ decomposition. The TGA analysis of the $LaMnO_3$ was in agreement with the DTA peaks showing distinct regions of weight loss corresponding to the temperature regions mentioned in the DTA, Fig 3(b). The XRD spectra of Lanthanum manganite solid phase was shown in Fig 4. The strongest peak was examined at (020) reflection as the 5th peak for all fabricated powders. The $La_{0.98}$ $Mn_{0.02}O_3$ was scanned through an angle 2θ from 10° to 70° and recorded as Fig 4. The surface of the sample was rotated by X-ray beam from Cu-fine focus tube. The applied voltage and current were maintained at 40 kV and 20mA. From XRD measurement, it was found that the orthorhombic phase of LMO powder was obtained at this temperature range 800°C to 1200°C there were six reflections on XRD profile and all reflection were consistent with that $LaMnO_3$ standard(JCPDF). Temperature control on FWHM and crystallite size of dominant (202) peak was observed for LMO powder. The demonstrated figure was shown in Fig 5. Fig 6 showed the XRD spectrum of LMO fibre on Al substrate. Except for the LMO peaks, no other diffraction peaks from randomly oriented grains or impurity phase were detected. The LMO fibre has a smooth surface and a good crystal structure. Inorder to study the morphology and size of the as-synthesized fibres, the prepared fibres were characterized by SEM, as shown in Figure 7.(a), (b), (c) (d) and (e). The surface of the composite nanofibres (ultra-fine fibres) was very smooth, and the diameter of the composite fibres was about 50nm at 800°C.

The lattice parameters, FWHM, crystallite size (G), and bond length (l) are listed in Table 1.

TABLE 1 Structural properties of $LaMnO_3$ sample

$La_{0.98}Mn_{0.02}O_3$ sample	**Structural Properties**	
	powder	**fibre**
Lattice Parameter, a (Å)	4.5484	5.8142
Lattice Parameter, b (Å)	5.2602	5.8429
Lattice Parameter, c (Å)	6.9399	7.9318
Bond – length (Å)	2.7285	3.4
FWHM (deg)	0.201	0.172
Crystallite –size (nm)	41.385	48.9

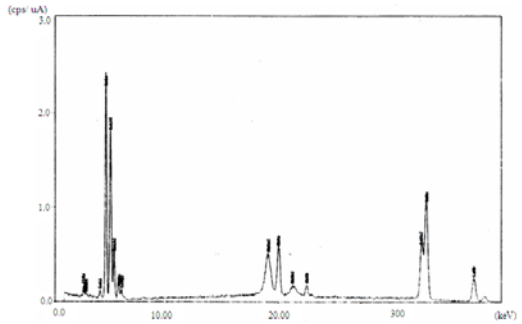

Fig.1 XRF patterns of starting $La_{0.98}$ $Mn_{0.02}O_3$ powder at 1000°C

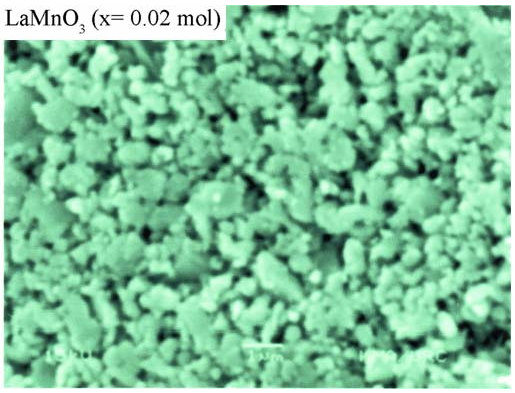

Fig.2 SEM image of lanthanum manganite $La_{0.98}$ $Mn_{0.02}O_3$ powder at 1000°C

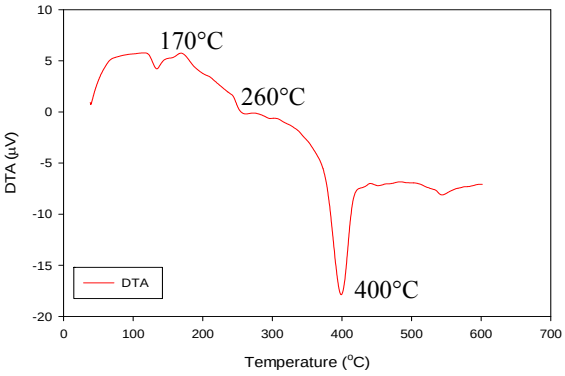

Fig. 3 (a) DTA analysis of $La_{0.98}$ $Mn_{0.02}O_3$ powder

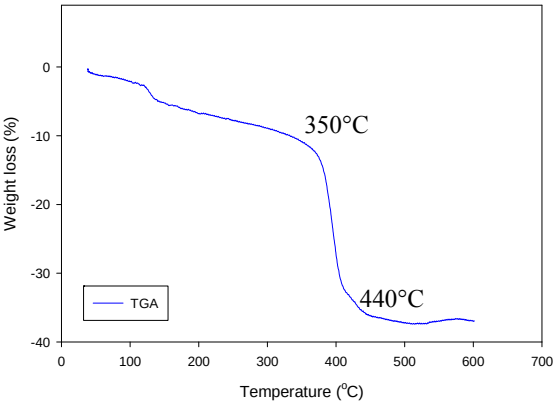

Fig.3 (b) TGA analysis of $La_{0.98}$ $Mn_{0.02}O_3$powder

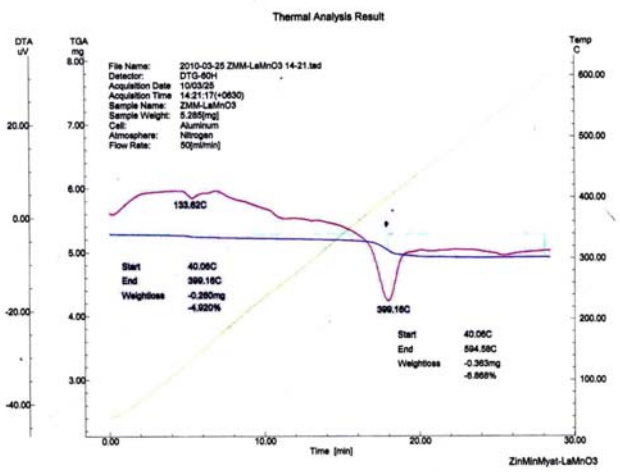

Fig. 3(c) TG-DTA analysis of $La_{0.98}Mn_{0.02}O_3$ powder

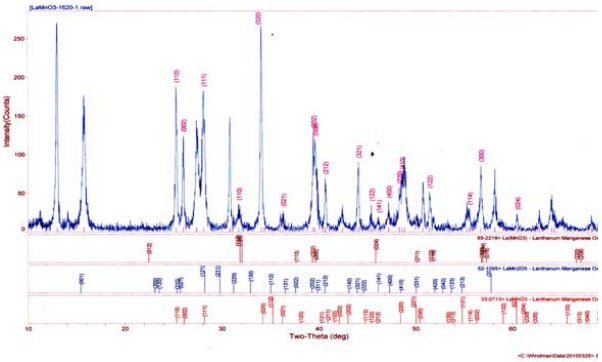

Fig.4 XRD patterns of $La_{0.98}$ $Mn_{0.02}O_3$ powders, annealing temperature at 1000°C

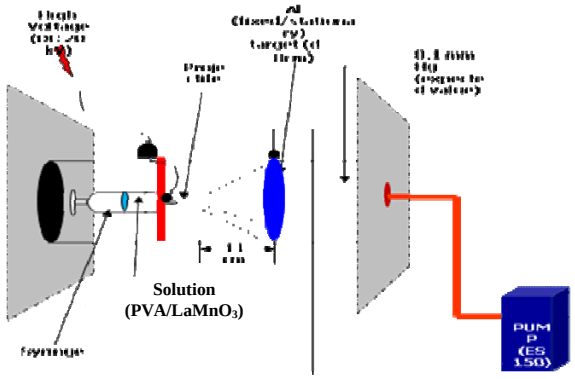

Fig. 5 Schematic diagram of electrospinning set up

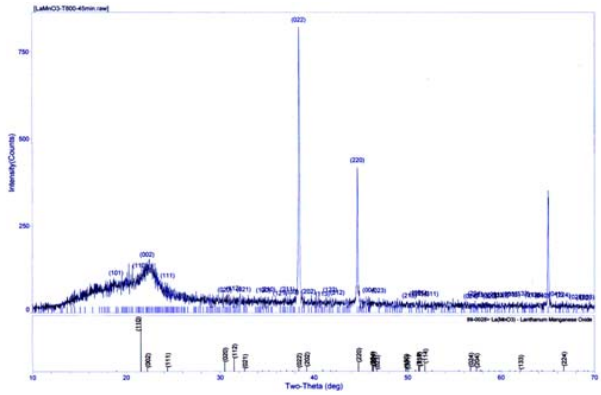

Fig. 6 XRD Patterns of $LaMnO_3$ fibres, annealing temperature at 800°C

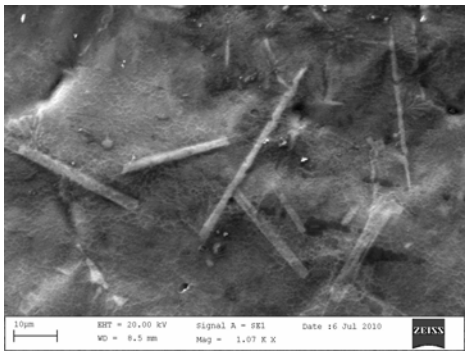

Fig. 7 (a) SEM image of lanthanum manganite $La_{0.98}Mn_{0.02}O_3$ fibre at 800°C

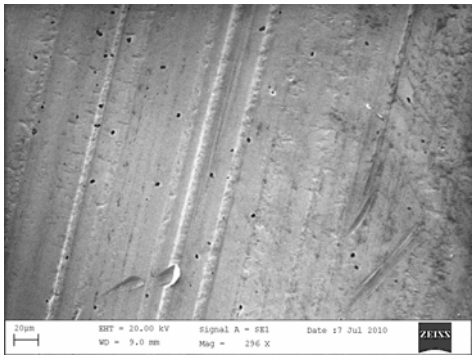

Fig. 7 (b) SEM image of lanthanum manganite $La_{0.98}Mn_{0.02}O_3$ fibre at 800°C

Fig. 7 (c) SEM image of lanthanum manganite $La_{0.98}Mn_{0.02}O_3$ fibre at 800°C

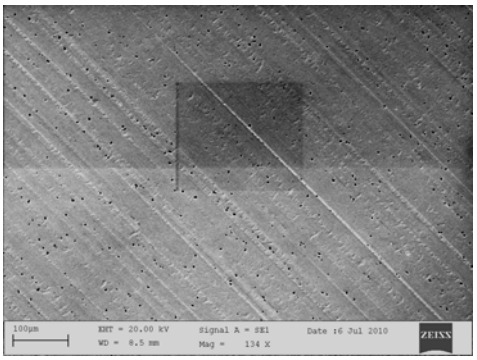

Fig. 7 (d) SEM image of lanthanum manganite $La_{0.98}Mn_{0.02}O_3$ fibre at 800°C

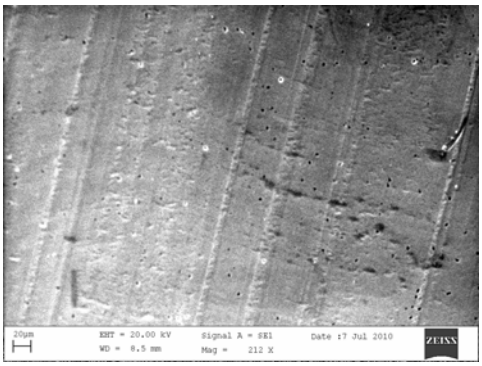

Fig. 7 (e) SEM image of lanthanum manganite $La_{0.98}Mn_{0.02}O_3$ fibre at 800°C

IV. CONCLUSION

Lanthanum manganite powder was fabricated by calcinations of the composite carbonate at 1000°C for thirty minutes. The grain size of the $LaMnO_3$ powder has clearly seen by SEM image. The surface has free from crack and pin holes. It is occurred that the resulting powders present a uniform morphology, being constructed by particles of spherical shapes. In the XRD analysis produces information on lattice parameters, bond-length, and FWHM and crystallite size regarding with the as-prepared sample and they are listed in Table 1. Phase pure $LaMnO_3$ were found to be very fine and fluffy in nature and produced crystalline $LaMnO_3$ at a lower temperature of 800°C XRD analysis revealed that the composite fibres were amorphous in structure. The crystal structure of the prepared $LaMnO_3$ was orthorhombic system with space group Pb nm. Structure formation of fibres was studied by using XRD analysis. SEM images indicated that the surface of the prepared composite fibres was smooth and the diameter of the composite fibres was about 50nm at 800°C $LaMnO_3$ ultra-fine fibres were successfully formed by electrospinning method.

ACKNOWLEDGEMENTS

The authors would like to thank Professor Dr Win Win Thar, PhD (YU), Head of Department of Physics, Yangon University for her kind permission to carry out this work.

REFERENCES

[1] Dong, X.T., Guo, Y.Z., D.C., etal (1994). Study of synthesis and electrical conductivity of $LaMnO_3$ ultrafine powders.*Rare Metal Mater. &Eng ., 23 (2),60.*

[2] http:// www. en. wikipedia. org / wiki / Lanthanum chloride

[3] http:// www. en. wikipedia. org / wiki / Maganese chloride.

[4] JSM–5610 LV2001"Scanning Electron Microscopy (SEM) Manual"

[5] http:// en.wikipedia.org / wiki / Scanning Electron Microscope.com