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Sucrose combustion synthesis of $La_xSr_{(1-x)}MnO_3$ ($x \leq 0.2$) powders

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Abstract

An energy efficient combustion synthesis has been used for the preparation of nanocrystalline LSM powder of composition $La_{1-x}Sr_xMnO_3$ ($x < 0.2$) using sucrose as a polymerisable fuel. Nitrate salt of La^{3+} and Sr^{2+} and acetate of Mn^{2+} were dissolved in water along with sucrose and concentrated by heating in to the form of a viscous resin which is then transformed in to macro porous foam by drying at 120 °C. Phase pure LSM has been obtained by combustion of these foams initiated with a matchstick in a set up fabricated in our laboratory. A minimum of 2 moles of sucrose is required for one mole of LSM ions for the formation of perovskite LSM phase. The LSM powder obtained by planetary milling of the combustion ash shows particle size in the range 0.1–6 μm with a D_{50} value ~0. 2 μm. The crystallite size calculated from XRD data using Scherer equation is in the range 13.12–17.9 nm. More than 97% TD has been achieved by cold compaction and sintering at of these powders.
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Keywords: A. Powder; E. Fuel cells; Combustion synthesis; Lanthanum manganite

1. Introducton

Solid oxide fuel cells (SOFC) are identified as clean, efficient and high capacity futuristic energy devices [1–3]. This instigates research in the area of novel synthetic methods for ceramic powders for cathode, anode interconnects and electrolyte materials used in SOFC. $La_{1-x}Sr_xMnO_3$ ($x < 0.2$) (LSM) powder has been widely used as cathode material in SOFC [1–5]. Solid state synthesis, emulsion process and self propagating high temperature synthesis have been reported for LSM synthesis. [6,7]. Recently, Aono et al. reported a preparation of nano sized un-doped lanthanum manganite by thermal decomposition of heteronuclear complexes of lanthanum and manganese with *N*,*N*′ bis(3hydroxy salicylidene) ethylene diamine [8].

Polymer precursor method provides reactive ceramic powders at reasonably low temperature [9]. In this method, metal ion solution containing polymeric or polymerisable organic molecule is heated to form a gel and then thermally decomposed to the ceramic powders. The metal ions are uniformly distributed in the polymer gel and they are attached to the polymer molecules through functional group such as OH and COOH present in the polymer structure. This method was first reported by Pechini using citric acid and ethylene glycol as the polymerisable organic molecules and later used by various authors for preparation of a large number of simple and mixed oxide powders [10–13]. Poly acrylic acid, polyvinyl alcohol and urea formaldehyde are other polymeric materials used for the synthesis of ceramic powders by this route [14–17].

Combustion synthesis is another powder synthesis route in which metal nitrate solution containing a fuel is heated in furnace at about 500 °C [18,19]. Urea and glycine are the commonly used fuels in combustion synthesis [18,19]. An auto ignition process using citric acid as fuel is also reported for synthesis of ceramic oxide powders [20]. Recently, sucrose has been used as complexing agent and fuel for the synthesis of α-alumina and magnesium aluminate [20–22]. Though sucrose is an inexpensive agricultural product, little attention is paid for its utilization as fuel for ceramic powder synthesis by combustion technique compared to citric acid

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and glycine. Present paper reports preparation of LSM powder by combining the principles of polymer precursor synthesis and combustion synthesis using sucrose as a polymerisable fuel.

2. Experimental

Lanthanum nitrate (99%, CDH, Delhi), strontium nitrate (99.9%, Merck, India), manganese acetate (99%, S.D. fine, India) and sucrose (Merck, India) used for this study were AR grade. Nitric acid (Merck, India) was used for pH adjustments. Distilled water was used for the preparation of solutions.

The flow chart for the process is shown in Fig. 1. Sucrose and stoichimetric amount of lanthanum nitrate, strontium nitrate and manganese acetate were dissolved in minimum quantity of water and the pH of the resulting solution was adjusted to 1.0 using nitric acid. This homogeneous solution is heated on a hot plate till it become a dark viscous resin. The resins were prepared at various LSM ions (La^{3+}, Sr^{2+} and Mn^{2+}): sucrose mole ratios ranging from 1:0.5 to 1:5. The resins were dried in a hot air oven at 120 °C. The TGA and DTA analysis of the dried samples were carried out in air at a heating rate of 10 °C/min in a thermal analyzer(Setsys 16/18, Setaram Scientific and Industrial Equipment, France).The dried resins were ignited in a set up fabricated in our laboratory(Fig. 4) and the ignition was initiated with a matchstick. The ashes obtained were analyzed for LSM phase formation in an X-ray difractometer (Philips analytical PW 1710) using Cu Kα radiation. The ash obtained after combustion was deagglomerated in a planetary ball mill using zirconia grinding media. Crystallite sizes of the powders were calculated from XRD data using Scherrer equation. Particle size analysis of the powders was carried out using Malvern Master size analyzer 2000. The deagglomerated powders were compacted in a hydraulic press at a pressure of 50 MPa and sintered at 1350 °C for 2 h. Densities of the sintered samples were measured by Archimedes principle. Microstructure of the ashes, deagglomerated powders and fractured surface of sintered samples were observed in a scanning electron microscope (LEO 1455).

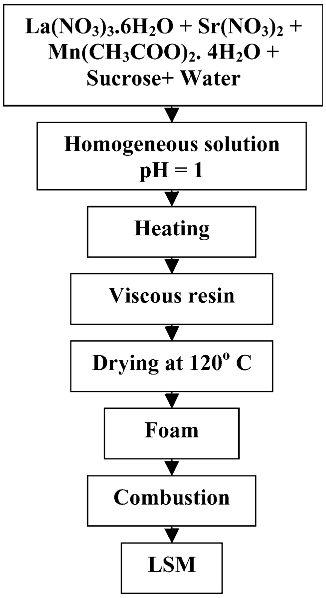

Fig. 1. Flow chart for sucrose combustion synthesis of LSM.

3. Results and discussion

Acidic solution (pH = 1) containing sucrose, lanthanum nitrate, strontium nitrate and manganese acetate on heating forms a dark viscous resin due to the polymerization of sucrose. This on drying at 120 °C undergoes foaming and the foam volume is found to be about 40 times the initial volume of the resin. The metal ions (La^{3+}, Sr^{2+} and Mn^{2+}) are likely to attach to the sucrose polymer structure by co-ordination through the hydroxyl groups and their distribution is expected to be uniform throughout the polymer [15]. Fig. 2 shows micrograph of a thin section of the foam observed under an optical microscope. The foam has thin walled reticulated microstructure. Most of the cells in the foam structure are in the size range 50–250 μm.

Fig. 3 shows the TGA–DTA plot of the foam sample prepared at LSM ions: sucrose mole ratio 1:2. Thermal decomposition takes place in two stages and burn out of organics is complete at 525 °C. A sharp exotherm observed in the temperature range 150–175 °C corresponding to the charring of sucrose polymer and a broad exotherm observed in the temperature range 350–525 °C is corresponding to the slow combustion of carbon. As the sucrose content in the foam increases the temperature for complete burn out of organics increases such that weight loss from foam prepared at LSM: sucrose mole ratio 1:5 is complete at 700 °C.

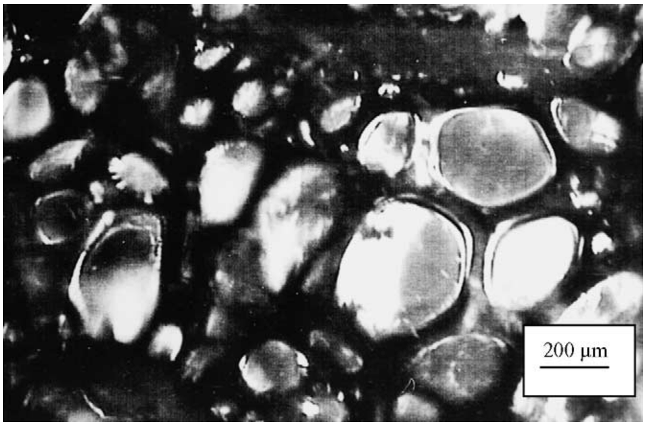

Fig. 2. Optical micrograph of a thin section of foam obtained by drying sucrose resin containing LSM ions (LSM ions: sucrose mole ratio1:2).

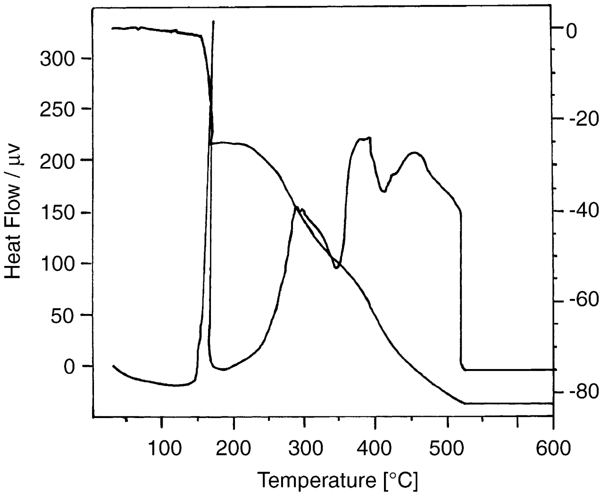

Fig. 3. TGA–DTA plot of foam sample obtained at LSM ions: sucrose mole ratio 1:2.

Fig. 4 shows drawing of the set up used for combustion of the foam. The set up consists of a 5 l cylindrical stainless steel vessel which is divided in to two compartments with a porous partition. The dried foam is charged in the upper compartment and air is passed from lower compartment through the porous partition. The outer wall of the steel vessel is covered with glass wool mat for thermal insulation. When ignited with a burning matchstick the foam catches fire due to its thin walled macro porous reticulated structure. The foams burn like a dry cellulose materials and the flame subsides in few minutes leaving a red hot mixture of carbon and other inorganics. The slow combustion of carbon continues till whole carbon gets exhausted. Time taken for completion of combustion is less than 1 h for 100 g LSM powder batch. The temperature of the contents rose to a maximum of 710 °C during combustion. The glass wool insulation minimizes heat loss and maintains the temperature above 600 °C through out the combustion process that would be conducive for LSM phase formation.

Calculations based on principles of propellant chemistry shows 0.5 mole sucrose is required for the combustion of sucrose–La, Sr, and Mn nitrate mixturer for formation of one mole LSM [23]. However, XRD analysis of the ashes obtained after combustion shows phase pure perovskite LSM formation at LSM ions: sucrose mole ratio 1:2. That is, 4 moles of sucrose is required for formation of one mole of phase pure LSM. Fig. 5 shows the XRD pattern of the ashes. This is further confirmed by the fact that the ash obtained from foam prepared at sucrose content lower than 1:2 composition shows a weight loss of more than 5% when heated at 700 °C compared to 0.3% weight loss in 1:2 composition. This indicates that heat generated by combustion is insufficient to decompose the salts completely at sucrose content lower than 1:2 composition. Also, the weight loss of 0.3% at 700 °C from the ash indicates that the removal of carbon is complete during the combustion process.

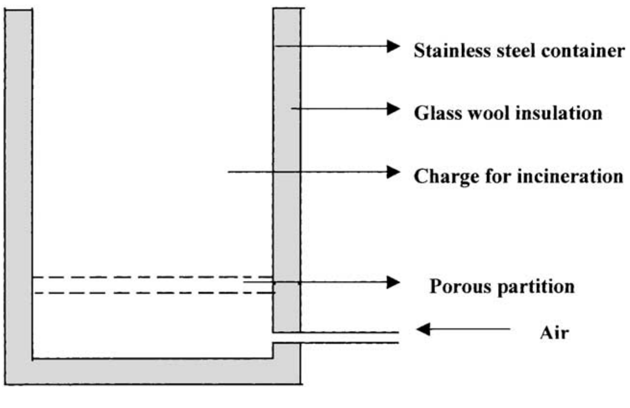

Fig. 4. Schematic drawing of the combustion set up.

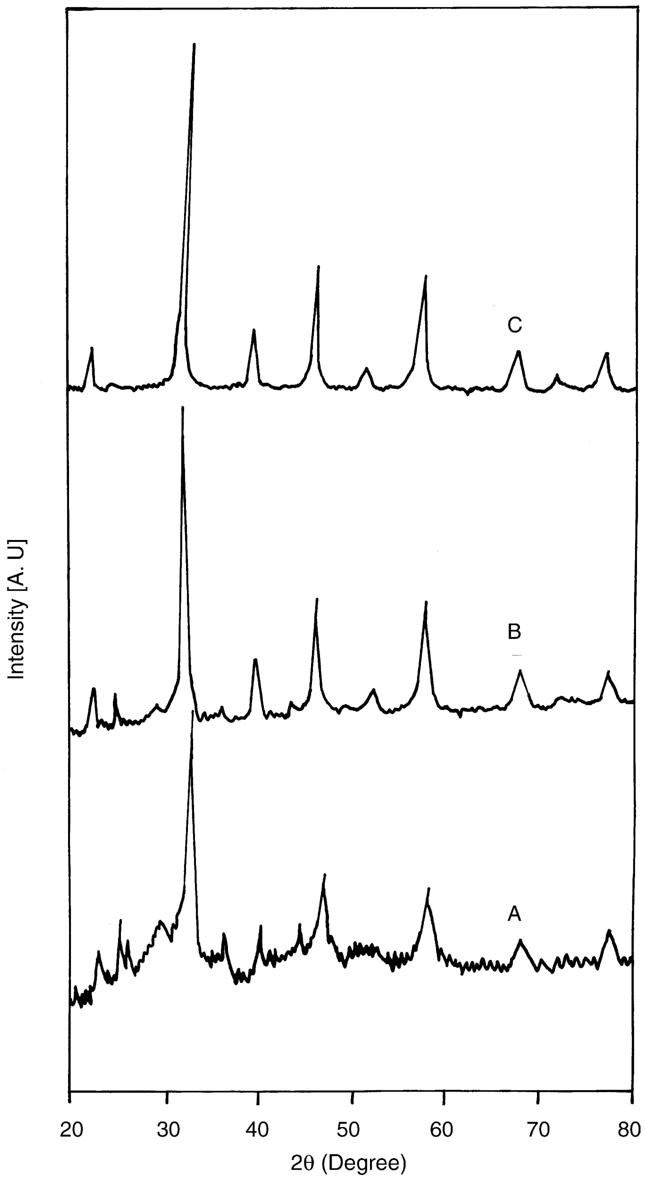

Fig. 5. XRD pattern of ashes obtained at various LSM ions: sucrose mole ratios (A, 1:0.5; B, 1:1; C, 1:2) showing phase pure LSM formation at 1:2 mole ratios.

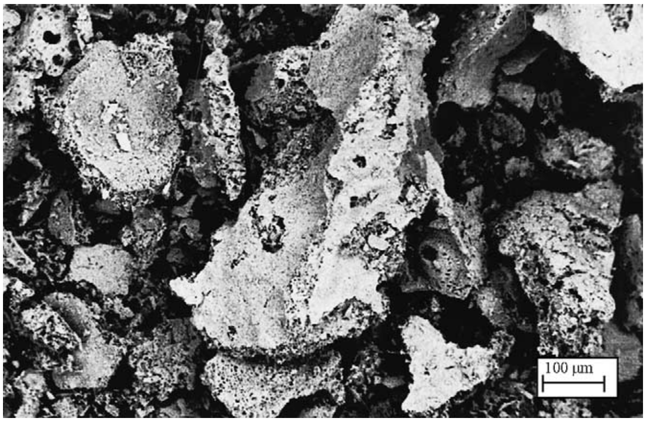

Fig. 6. SEM photograph of the ash obtained at LSM ions: sucrose mole ratio 1:2.

In combustion synthesis metal nitrate–fuel mixture is heated in a muffle furnace above 500 °C to initiate the combustion reaction. In auto ignition process the metal nitrate–citric acid mixture is first heated in hot plate (~250 °C) and the resulting charred powder is then heated in muffle furnace at 600 °C for removal of carbon and for formation of the crystalline phase. Our experience in synthesizing yttria stabilized zirconia powder in 100 g level by auto ignition process is that removal of carbon from the charred powder takes more than six ours in a muffle furnace at 600 °C. The pechini type polymer precursor process also produces amorphous powders and requires further calcination for phase formation. That is, in these processes relatively high amount of electrical energy is consumed. In the present work, the heat of combustion is efficiently utilized for phase formation with out further calcination of the powder by carrying out the combustion reaction in the special set up.

Fig. 6 shows SEM photograph of the ash obtained at LSM ions: sucrose mole ratio 1:2. The ash consists of porous and loose aggregates of LSM fine particles and can be easily broken down in to primary particles. The powders prepared by planetary milling of the ashes obtained at LSM ions: sucrose mole ratio 1:2–1:5 show almost same particle size distributions. The particle size observed is in the range 0.1–6 µm. The D_{50} values of the powders are in the range from 0.21 to 0.24 µm at LSM ions: sucrose mole ratio in the range 1:2–1:5. Only small fraction (<6%) of particle is having size higher than 1 µm. Fig. 7 shows the particle size distribution of LSM powder prepared at LSM ions: sucrose mole ratio 1:2. The crystallite size calculated from XRD data using Scherer equation shows the powders are nanocrystalline and the crystallite size increases from 13.1 to 17.9 nm when the LSM ions: sucrose mole ratio changes from 1:2 to 1:5. The tap density of the powders measured were showing irregular trend and were observed in the range 19.23–21.7% TD. D_{50} value, crystallite size and tap density of powders were given in Table 1. SEM microstructure of the LSM powder is shown in Fig. 8.

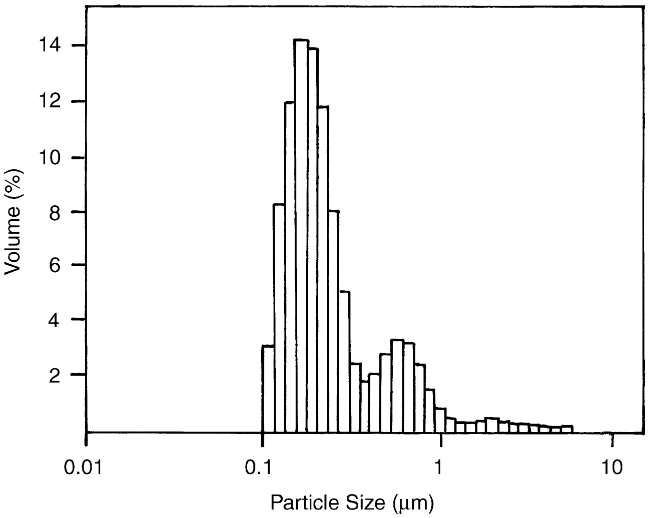

Fig. 7. Particle size distribution of LSM powder prepared at LSM ions: sucrose mole ratio 1:2.

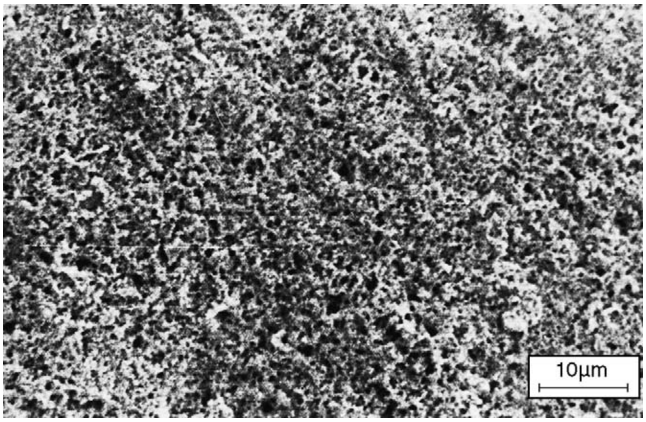

Fig. 8. SEM micrograph of LSM powder obtained by sucrose combustion method.

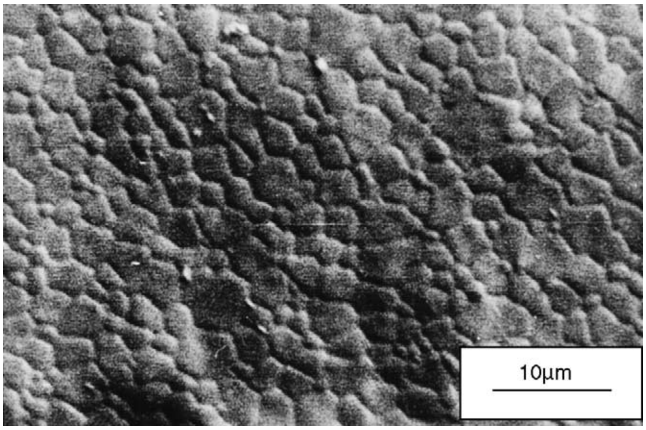

Fig. 9. SEM microstructure of fractured surface of sintered LSM sample.

Table 1
Characteristics of LSM powders prepared at various LSM ions: sucrose mole ratios

LSM ions: sucrose mole ratio	Crystallsite size from XRD data (nm)	D_{50} value (μm)	Tap density (%TD)	Density of samples sintered at 1350 °C (%TD)
1:2	13.12	0.22	21.97	97.50
1:3	14.85	0.21	20	97.52
1:4	15.72	0.21	20.46	97.3
1:5	17.9	0.24	19.23	97.6

The LSM powder compacts sintered to density >97% TD. The variation of sintered density with LSM ions: sucrose mole ratio is in close range and the density values are given in Table 1. Fig. 9 show SEM micrograph of fractured surface of a sintered LSM sample. The sintered sample showed dense microstructure without any inter granular or intra granular porosity.

4. Conclusions

A sucrose combustion process has been developed for phase pure nanocrystalline (13.12–19.7 nm) LSM powders. Temperature for LSM phase formation is attained outside a furnace by mere combustion of macro porous reticulated foams obtained by drying a viscous resin prepared by heating aqueous solution containing lanthanum nitrate, strontium nitrate, manganese acetate and sucrose. A minimum of 2 mole sucrose is required for 1 mole LSM ions for formation of phase pure LSM. The LSM powders prepared shows particle size in the range 0.1–0 6 μm with a D_{50} value ~0.2 μm. The powder compacts sintered to >97% TD at 1350 °C and sintered samples show dense microstructure.

Acknowledgements

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