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Preparation, characterization and the standard enthalpy of formation of $La_{0.95}MnO_{3+\delta}$ and $Sm_{0.95}MnO_{3+\delta}$

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ABSTRACT

Among the perovskites, the rare earth manganites find application in several electrochemical devices because of their enhanced thermodynamic stability. In this paper, we present the results obtained on the preparation and characterization of $La_{0.95}MnO_{3+\delta}$ and $Sm_{0.95}MnO_{3+\delta}$ which were prepared by the solid state and sol–gel methods. XRD characterization of the manganites indicated that the crystal structure depends on the method of preparation and heat treatments. The ratio of Mn^{3+} to Mn^{4+} in these samples also depended on the method of preparation and heat treatments, as indicated by thermogravimetric (TG) and temperature programmed reduction (TPR) studies in Ar + 5% H_2 atmosphere. The standard molar enthalpy of formation, which is a measure of the thermodynamic stability of these compounds were determined using an isoperibol calorimeter.

1. Introduction

Ceramic oxides with the perovskite structure ABO_3 where A is a rare-earth element and B is a transition metal, are of great practical significance in various electrochemical applications such as solid oxide fuel cells (SOFC), gas sensors, catalysts and oxygen separation membranes. Among these oxides, the manganites find application in several devices because of their enhanced thermodynamic stability.

Thermodynamic properties of $LaMnO_3$ have been reported in literature [1–4] using solid electrolyte galvanic cell or high temperature calorimetric techniques. There is considerable variation on the values of enthalpy of formation of $LaMnO_3$ reported by these investigators. In these investigations, $LaMnO_3$ has been prepared by solid state method. The rare earth manganites, prepared by conventional solid state route [5,6] often yield inhomogeneous products. In the case of lanthanum manganites, the phase pure product is obtained by heating to high temperatures of the order of 1500 K or above for prolonged periods and one ends up with nearly stoichiometric $LaMnO_3$ which has only 2–3% of Mn^{4+} concentration. In rare earth deficient manganites, the subsequent deficit charge is compensated by a valence change of transition metal ions, and also, by the creation of oxygen vacancies. The interesting properties of the manganites are due to the presence of Mn^{4+} ions. It has been established that rare earth deficient $LaMnO_3$ exhibits better sintering ability [7], higher conductivity [8] and inertness towards other cell components of SOFC [9]. Moreover, the concentration of Mn^{4+} species can be enhanced by adopting suitable, low temperature, wet chemical preparation routes.

In this paper, we present the results obtained on the preparation, characterization and thermodynamic stability of rare earth deficient manganites, $La_{0.95}MnO_{3+\delta}$ and $Sm_{0.95}MnO_{3+\delta}$ which were prepared by the sol–gel method. The compounds were characterized by XRD and their thermodynamic stability was determined by isoperibol calorimetry. The rare earth manganites prepared by the conventional solid state route were also characterized by XRD analysis and compared with the sample prepared by sol–gel method.

2. Experimental

2.1. The preparation of $La_{0.95}MnO_{3+\delta}$ and $Sm_{0.95}MnO_{3+\delta}$ by different routes

2.1.1. Solid state route

$La_{0.95}MnO_{3+\delta}$ was prepared by heating thoroughly ground mixtures of La_2O_3 (Loba Chemie, 99.9%) and $MnCO_3$ (Aldrich, 99.9%) in stoichiometric amounts. La_2O_3 used was preheated at 900 °C in order to remove absorbed moisture and CO_2. The mixture was heated in a platinum boat at 800 °C in air for 48 h with one intermittent grinding. $Sm_{0.95}MnO_{3+\delta}$ was also prepared by the solid state route by adopting a similar procedure, using Sm_2O_3 (Loba Chemie, 99.9%) and $MnCO_3$ (Aldrich, 99.9%). Subsequently, the samples were heat treated at 1400 °C for 3 h.

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2.1.2. *Sol–gel route*

$La_{0.95}MnO_{3+\delta}$ was prepared by sol–gel route using urea as the gelification agent. $La(NO_3)_3{\cdot}6H_2O$ (Fluka, 99.9%) and $Mn(NO_3)_2{\cdot}6H_2O$ (Fluka, 99.9%) were used as the starting material. The initial concentrations were 0.19 M in La^{3+}, 0.2 M in Mn^{2+} and the urea concentration was fixed at $\Phi = 10$, with $\Phi = (\mathrm{urea})/(La^{3+} + Mn^{2+})$. The solvent (water in this case) was evaporated directly on a hot plate with continuous stirring at temperatures ranging between 120 °C and 130 °C. On cooling, a yellow gel was formed, which was decomposed in an oven at 250 °C in air for 3 h, yielding a fairly porous precursor. After milling in an agate mortar the precursor was calcined at 600 °C for 24 h. The second heat treatment was for 48 h at 800 °C. $Sm_{0.95}MnO_{3+\delta}$ was prepared by sol–gel route using a similar method, using $Sm(NO_3)_3{\cdot}6H_2O$ (Fluka, 99.9%) and $Mn(NO_3)_2{\cdot}6H_2O$ (Fluka, 99.9%). Samples prepared by sol–gel route were also heat treated at 1400 °C for 3 h.

2.2. *Characterization of $La_{0.95}MnO_{3+\delta}$ and $Sm_{0.95}MnO_{3+\delta}$*

The unit cell parameter and the phase purity were determined by recording powder XRD patterns of all the samples on a Philips X-ray diffractometer (PW 1710) with Ni filtered Cu K_α radiation and using silicon as an external standard. These patterns were indexed to generate their lattice dimensions using POWD program [10].

The cationic composition of all the samples at the end of thermal treatments were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The quantity of excess oxygen δ was determined by thermogravimetry by recording TG scans on TG-DT 30 Shimadzu thermobalance in H_2 atmosphere (5% in Ar) with sample size of ~200 mg and a heating rate of 10 °C min^{-1}. Prior to TG run the sample was heated from room temperature to 800 °C in argon atmosphere and it was cooled to 200 °C in the same atmosphere for the removal of any adsorbed gases.

Temperature programmed reduction (TPR) studies were carried out on a TPDRO-1100 analyzer (Thermoquest, Italy) using H_2 (5%) + Ar gas mixture. A heating rate of 6 °C min^{-1} was employed and the experiments were carried out in the range of 27–1000 °C. The effluents were passed through a soda lime trap to remove any reaction products and H_2 was monitored with a thermal conductivity detector. Before TPR run all the samples were pretreated in argon atmosphere flow (20 ml/min) at 300 °C for 3 h and then cooled to room temperature to remove any absorbed gases from the samples.

The quantity of excess oxygen δ was also determined by reducing Mn^{4+} component with a known excess of ferrous ammonium sulphate in sulphuric acid medium. The excess ferrous concentration was estimated by redox titration with standard potassium dichromate solution in the presence of diphenylamine indicator.

The redox titration method could be used for only those samples prepared by the sol–gel route and heat treated at 800 °C. It was not possible to dissolve the samples prepared by solid state route or the sol–gel route and sintered at 1400 °C in ferrous ammonium sulphate in sulphuric acid medium to evaluate the quantity of excess oxygen (δ).

2.3. *Calorimetric studies*

The $La_{0.95}MnO_{3+\delta}$ prepared by solid state route could not be dissolved in an appropriate solvent at room temperature as required for the isoperibol calorimetry. Moreover, $Sm_{0.95}MnO_{3+\delta}$ prepared by solid state route was not single phase. Therefore, the samples prepared by the sol–gel route were used for the calorimetric studies. The enthalpies of dissolution $La_{0.95}MnO_{3+\delta}(s)$ and $Sm_{0.95}MnO_{3+\delta}(s)$ were measured in an isoperibol calorimeter operated at 298.15 K. The construction and operation of the calorimeter is similar to the one described by Athavale et al. [11]. Details about the calibration of the calorimeter with KCl and TRIS are given in [12,13]. The sample was weighed and introduced into a glass bulb which was then thermally equilibrated in the calorimetric solution. The calorimetric solution i.e., the solvent for dissolution of $La_{0.95}MnO_{3+\delta}$ was 0.150 dm^3 of a 1:1 mixture of 0.1 mol dm^{-3} of $FeSO_4(NH_4)_2SO_4$ + 4.00 mol dm^{-3} of H_2SO_4 and that for $Sm_{0.95}MnO_{3+\delta}$ was 0.150 dm^3 of a 1:1 mixture of 0.2 mol dm^{-3} of $FeSO_4(NH_4)_2SO_4$ + 4.00 mol dm^{-3} of H_2SO_4. The glass bulb was broken to introduce the sample into the solvent when a steady state signal from the thermistor probe was obtained on the strip chart recorder. The energy required to increase the temperature of the calorimeter loaded with the solvent by a given value (energy equivalent of the calorimeter) was determined before every measurement by electrical calibration. The enthalpies of dissolution of $La_2O_3(s)$, $Sm_2O_3(s)$, $MnSO_4(s)$, $H_2O(l)$, $H_2SO_4(l)$ and $H_2O_2(l)$ in the respective solvents were also measured. Using these experimental values and other auxiliary data from literature, the enthalpy of formation of $La_{0.95}MnO_{3+\delta}$ and $Sm_{0.95}MnO_{3+\delta}$ were determined.

3. Results and discussions

3.1. *Characterization*

The XRD patterns of the compounds $La_{0.95}MnO_{3+\delta}$ and $Sm_{0.95}MnO_{3+\delta}$ prepared through solid state and sol–gel routes and heat treated at 800 °C for 48 h are presented in Fig. 1. All these samples were subsequently heated to 1400 °C and quenched and their XRD patterns are represented in Fig. 2. The $La_{0.95}MnO_{3+\delta}$ samples from solid state and sol–gel routes heated at 800 °C, crystallize in rhombohedral form. $Sm_{0.95}MnO_{3+\delta}$ from solid state route and heated at 800 °C shows impurity phases while that from sol–gel route and similarly heat treated crystallizes in pure orthorhombic form. The $La_{0.95}MnO_{3+\delta}$ prepared by solid state synthesis and heated upto 1400 °C and then quenched crystallizes in rhombohedral form, while the sol–gel sample crystallizes in orthorhombic form under the similar treatment. $Sm_{0.95}MnO_{3+\delta}$ from solid state or sol–gel routes and treated at 1400 °C crystallizes in orthorhombic form. These patterns have been indexed, the lattice parameters and the cell volume are given in Tables 1 and 2. It is clear that the lattice parameters and the cell volume depend on the δ value. The δ value indicates the excess amount of oxygen. Since the ionic radii of

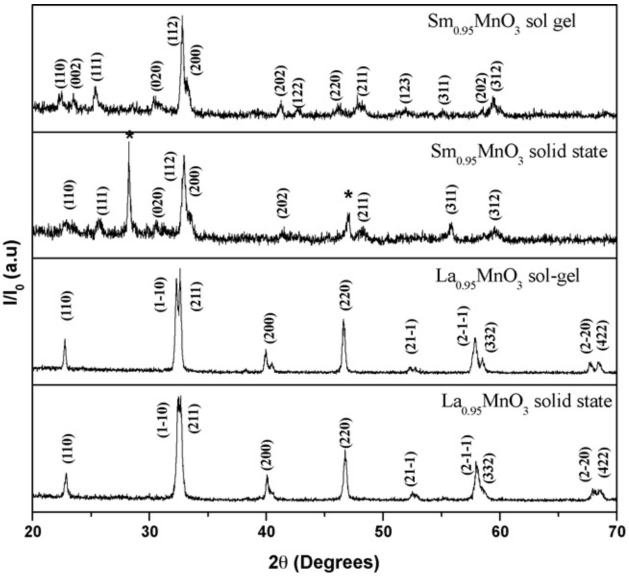

Fig. 1. XRD patterns of $La_{0.95}MnO_{3+\delta}$ and $Sm_{0.95}MnO_{3+\delta}$ prepared by solid state and sol–gel routes which were heated at 800 °C for 48 h (*Sm_2O_3).

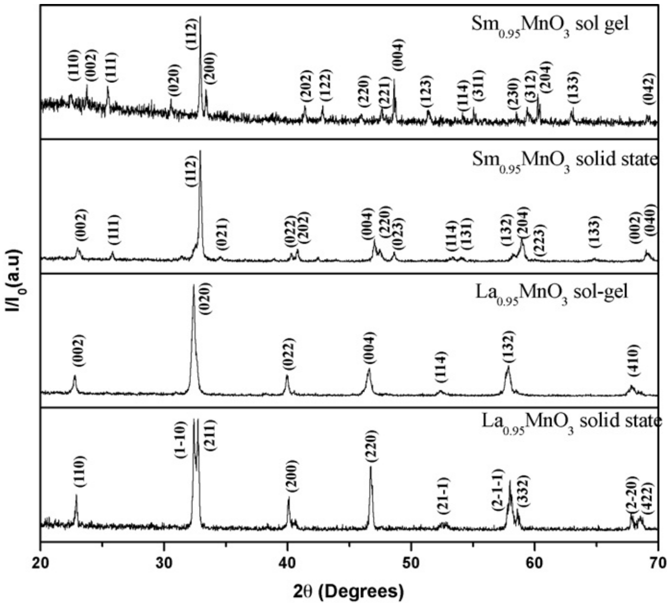

Fig. 2. XRD patterns of $La_{0.95}MnO_{3+\delta}$ and $Sm_{0.95}MnO_{3+\delta}$ prepared by solid state and sol–gel routes which were quenched at 1400 °C.

O^{2-} (1.32 Å) [14] is large, with increase in δ value there is increase in lattice parameters and the cell volume. The $La_{0.95}MnO_{3+\delta}$ and $Sm_{0.95}MnO_{3+\delta}$ prepared by sol–gel route were heated at different temperatures in order to study the crystallite size. The crystallite size d_{XRD} of the calcined powders was estimated using the Scherrer's formula.

$$d_{XRD} = \frac{0.9\lambda}{(\beta\cos\theta)}$$

where λ is the wavelength of the X-rays and θ is the scattering angle of the main reflection (reflection 2 1 1 in case of $La_{0.95}MnO_{3+\delta}$ and reflection 1 1 2 in case of $Sm_{0.95}MnO_{3+\delta}$) [15]. High grade silicon powder was used as standard to account for instrument broadening correction. For $La_{0.95}MnO_{3+\delta}$ prepared by solid state route, the crystallite size calculated from the pattern at 800 °C is 69 nm. For $La_{0.95}MnO_{3+\delta}$ prepared by sol–gel route, the crystallite sizes calculated from the patterns at 600 °C and 800 °C are 18 nm and 44 nm, respectively, while that for $Sm_{.95}MnO_{3+\delta}$ prepared by sol–gel route is 71 nm at 800 °C.

Table 3
Elemental analysis of $Ln_{0.095}MnO_{3+\delta}$.

Compounds	%La content		%Mn content		δ[b]	
	Obs.[a]	Calc.	Obs.[a]	Calc.	TGA	Redox titration
Solid state route (1400 °C)						
$La_{0.95}MnO_{3+\delta}$	55.3	56.1	22.7	23.3	0.01	–
$Sm_{0.95}MnO_{3+\delta}$	57.9	58.4	22.1	22.5	−0.075	–
Sol–gel route (800 °C)						
$La_{0.95}MnO_{3+\delta}$	55.0	56.0	22.6	23.3	0.06	0.05
$Sm_{0.95}MnO_{3+\delta}$	56.9	57.8	21.8	22.2	0.09	0.10
Sol–gel route (1400 °C)						
$La_{0.95}MnO_{3+\delta}$	55.0	56.0	22.6	23.3	0.04	–
$Sm_{0.95}MnO_{3+\delta}$	57.4	58.1	23.1	22.3	0.01	–

[a] The standard deviation (SD) for the determination of cationic composition is ±2%.
[b] The SD for δ is ±1%.

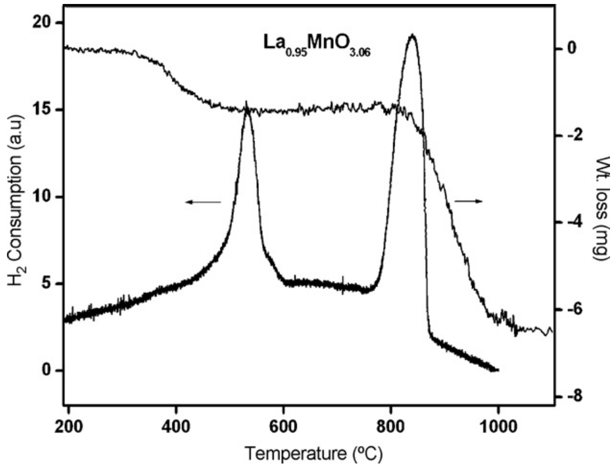

Fig. 3. TG and TPR profiles of the reduction carried out in Ar + 5%H_2 for $La_{0.95}MnO_{3+\delta}$ prepared by sol–gel route and heated at 800 °C. (Sample size for TG curve = 151.6 mg).

The Ln:Mn ratio of $La_{0.95}MnO_{3+\delta}$ and $Sm_{0.95}MnO_{3+\delta}$ was determined by inductively coupled plasma atomic emission spectroscopy and is given in Table 3. The quantity of excess oxygen δ was determined by thermogravimetry and also by redox titration in some cases and are given in Table 3.

The thermogravimetry plots of the samples (~200 mg) heated in Ar + 5% H_2 atmosphere, in the temperature interval of 25–1000 °C, at a heating rate of 10 °C min^{-1} are shown in Figs. 3 and 4 for $La_{0.95}MnO_{3.06}$ and $Sm_{0.95}MnO_{3.09}$ (samples prepared by sol–gel method and annealed at 800 °C), respectively, along with the corresponding TPR plots.

Table 1
Lattice parameters of $La_{0.95}MnO_{3+\delta}$ and $Sm_{0.95}MnO_{3+\delta}$ prepared by different routes. All these samples have been heated at 800 °C for 48 h.

Compound	Method of preparation	Symmetry	Lattice parameters			Cell volume (Å^3)
			a (Å)	*b* (Å)	*c* (Å)	
$La_{0.95}MnO_{3+\delta}$	Solid State	Rhombohedral	5.518(0)	–	13.350(8)	351.9
	Sol–gel	Rhombohedral	5.535(0)	–	13.368(5)	353.5
$Sm_{0.95}MnO_{3+\delta}$	Sol–gel	Orthorhombic	5.355(3)	5.775(7)	7.506(6)	232.1

Table 2
Lattice parameters of $La_{0.95}MnO_{3+\delta}$ and $Sm_{0.95}MnO_{3+\delta}$ prepared by different routes. All these samples have been heated to 1400 °C and quenched.

Compound	Method of preparation	Symmetry	Lattice parameters			Cell volume (Å^3)
			a (Å)	*b* (Å)	*c* (Å)	
$La_{0.95}MnO_{3+\delta}$	Solid state	Rhombohedral	5.530(0)	–	13.347(7)	352.6
	Sol–gel	Orthorhombic	5.536(3)	5.737(7)	7.823(8)	248.5
$Sm_{0.95}MnO_{3+\delta}$	Solid state	Orthorhombic	5.391(1)	5.509(2)	7.716(1)	229.2
	Sol–gel	Orthorhombic	5.369(9)	5.840(9)	7.480(8)	234.5

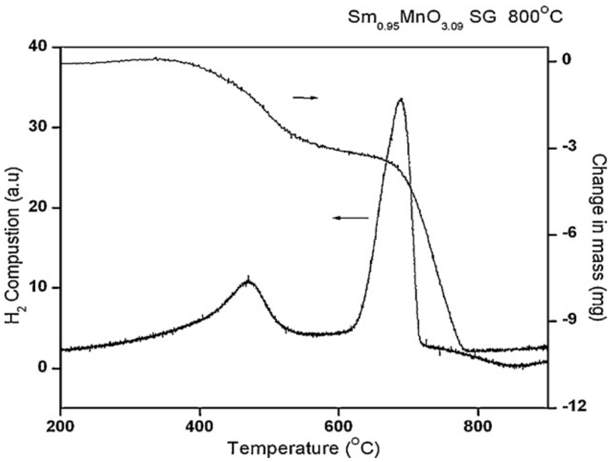

Fig. 4. TG and TPR profiles of reduction carried out in Ar + 5%H_2 for $Sm_{0.95}MnO_{3+\delta}$ prepared by sol–gel route and heated at 800 °C. (Sample size for TG curve = 233.05 mg).

Similar TG and TPR plots were obtained for $La_{0.95}MnO_{3+\delta}$ and $Sm_{0.95}MnO_{3+\delta}$ (samples prepared by solid state method or sol–gel method and annealed at 1400 °C) in order to derive the oxygen non stoichiometry δ for these samples.

The TG results for $La_{0.95}MnO_{3.06}$ and $Sm_{0.95}MnO_{3.09}$ are summarized in Table 4. The two distinct steps of decomposition observed in TG and TPR profiles (Figs. 3 and 4) can be attributed to the following scheme of decomposition:

$$La_{0.95}Mn_{0.73}{}^{3+}Mn_{0.27}{}^{4+}O_{3.06} \rightarrow La_{0.95}Mn^{3+}O_{2.925} \rightarrow (0.95/2)La_2O_3 + MnO \qquad (1)$$

$$Sm_{0.95}Mn_{0.67}{}^{3+}Mn_{0.33}{}^{4+}O_{3.09} \rightarrow Sm_{0.95}Mn^{3+}O_{2.925} \rightarrow (0.95/2)Sm_2O_3 + MnO \qquad (2)$$

Reactions (1) and (2) have been used for deriving the oxygen non stoichiometry δ reported in Table 3.

3.2. Calorimetric studies

From Tables 1–3, it is evident that the structure and stoichiometry of $La_{0.95}MnO_{3+\delta}$ and $Sm_{0.95}MnO_{3+\delta}$ depend on the method of preparation (solid state or sol–gel) and the annealing temperature (800 °C or 1400 °C). It was observed that $La_{0.95}MnO_{3+\delta}$ and $Sm_{0.95}MnO_{3+\delta}$ prepared by sol–gel route and annealed at 800 °C could only be dissolved in a suitable solvent at room temperature, as required by the isoperibol calorimeter used in this study.

The results of the enthalpies of dissolution of $La_{0.95}MnO_{3.06}(s)$, $La_2O_3(s)$ and $MnSO_4(s)$ in 0.150 dm^3 of a 1:1 mixture of 0.1 mol dm^{-3} of $FeSO_4(NH_4)_2SO_4$ + 4.00 mol dm^{-3} of H_2SO_4 are given in Table 5 and those of $Sm_{0.95}MnO_{3.09}(s)$, $Sm_2O_3(s)$ and $MnSO_4(s)$ in 0.150 dm^3 of a 1:1 mixture of 0.2 mol dm^{-3} of $FeSO_4(NH_4)_2SO_4$ + 4.00 mol dm^{-3} of H_2SO_4 are given in Table 6. In Table 4, m denotes the mass of the sample dissolved, ΔH is the measured energy change and $\Delta_{sol}H_m$ is the molar enthalpy of dissolution. The thermochemical cycle from which the standard molar enthalpies of formation of $La_{0.95}MnO_{3.06}(s)$ and $Sm_{0.95}MnO_{3.09}(s)$ have been derived are given in Tables 7 and 8, respectively.

Table 4
Thermogravimetric analysis of $La_{0.95}MnO_{3.06}$ and $Sm_{0.95}MnO_{3.09}$ prepared by sol–gel route heated at 800 °C.

Compound	Weight loss			Moles of O_2 lost
	Temperature range (°C)	Obs. (mg)	Cal. (mg)	
$La_{0.95}MnO_{3.06}$ (151.6 mg)	295–500	1.41	1.39	0.0675
	835–996	5.09	5.14	0.25
	295–996	6.50	6.53	0.3175
$Sm_{0.95}MnO_{3.09}$ (233.05 mg)	370–540	2.69	2.48	0.0825
	545–790	7.27	7.52	0.25
	370–790	9.96	10.01	0.3325

Table 5
The molar enthalpies of dissolution of $La_{0.95}MnO_{3.06}(s)$, $La_2O_3(s)$ and $MnSO_4(s)$ in 0.150 dm^3 of the solvent (0.1 mol dm^{-3} $FeSO_4(NH_4)_2SO_4$ + 4.0 mol dm^{-3} of H_2SO_4) at T = 298.15 K; m denotes the mass of the sample dissolved; ΔH is the measured energy change and $\Delta_{sol}H_m$ is the molar enthalpy of solution.

Solute	m (solute) (g)	ΔH (J)	$\Delta_{sol}H_m$ (kJ mol^{-1})
$La_{0.95}MnO_{3.06}(s)$ mol. wt. = 235.86	0.0306	−39.14	−301.5
	0.0374	−49.14	−309.7
	0.0553	−73.64	−313.9
	0.0345	−45.49	−310.8
	0.0487	−62.76	−303.8
Average			−307.9 ± 5.1
$La_2O_3(s)$ mol. wt. = 325.82	0.0767	−111.79	−474.9
	0.0620	−89.53	−470.5
	0.1192	−172.44	−471.3
	0.1648	−239.50	−473.5
	0.0677	−98.43	−473.7
Average			−472.8 ± 1.8
$MnSO_4(s)$ mol. wt. = 151.00	0.1282	−25.53	−30.1
	0.1260	−23.52	−28.2
	0.1832	−34.74	−28.6
	0.0989	−18.44	−28.2
	0.2416	−46.94	−29.3
Average			−28.9 ± 0.8

The experimentally measured values have been combined with other auxiliary data such as the standard enthalpies of formation of $La_2O_3(s)$ [16], $Sm_2O_3(s)$ [16], $MnSO_4(s)$ [16], $H_2O_2(l)$ [17], $H_2SO_4(l)$ [17] and $H_2O(l)$ [18] to derive the standard molar enthalpy of formation of $La_{0.95}MnO_{3.06}(s)$ and $Sm_{0.95}MnO_{3.09}(s)$ which works out to be −1419 ± 7 kJ mol^{-1} and −1426 ± 7 kJ mol^{-1}, respectively.

Table 6
The molar enthalpies of dissolution of $Sm_{0.95}MnO_{3.09}(s)$, $Sm_2O_3(s)$ and $MnSO_4(s)$ in 0.150 dm^3 of the solvent (0.2 mol dm^{-3} $FeSO_4(NH_4)_2SO_4$ + 4.0 mol dm^{-3} of H_2SO_4) at T = 298.15 K; m denotes the mass of the sample dissolved; ΔH is the measured energy change and $\Delta_{sol}H_m$ is the molar enthalpy of solution.

Solute	m (solute) (g)	ΔH (J)	$\Delta_{sol}H_m$ (kJ mol^{-1})
$Sm_{0.95}MnO_{3.09}(s)$ mol. wt. = 247.21	0.0868	−108.18	−308.2
	0.0623	−79.31	−314.8
	0.0491	−61.37	−309.1
	0.0444	−55.64	−309.9
	0.0548	−67.24	−303.4
Average			−309.1 ± 4.1
$Sm_2O_3(s)$ mol. wt. = 348.72	0.0759	−98.01	−450.3
	0.0549	−70.56	−448.2
	0.0676	−86.78	−447.7
	0.0653	−83.86	−447.8
	0.0708	−91.97	−453.0
Average			−449.4 ± 2.3
$MnSO_4(s)$ mol. wt. = 151.00	0.1293	−26.04	−30.4
	0.1293	−26.56	−31.0
	0.2711	−51.87	−28.9
	0.3772	−77.79	−31.1
	0.1587	−31.92	−30.4
Average			−30.4 ± 0.9

Table 7
Reaction scheme for the standard molar enthalpy of formation of $La_{0.95}MnO_{3.06}(s)$ (sln = 0.150 dm^3 of 0.1 mol dm^{-3} $FeSO_4(NH_4)_2SO_4$ + 4.0 mol dm^{-3} of H_2SO_4) at 298.15 K. $\Delta H_{12} = -\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7 - \Delta H_8 - \Delta H_9 + \Delta H_{10} + \Delta H_{11}$.

Reaction	ΔH_m (kJ mol^{-1})
(1) $La_{0.95}MnO_{3.06}(s) + [1.27\ FeSO_4 + 3.06\ H_2SO_4](sln) = [0.475\ La_2(SO_4)_3 + MnSO_4 + 0.635\ Fe_2(SO_4)_3 + 3.06\ H_2O](sln)$	−307.9 ± 5.1
(2) $0.475\ La_2O_3(s) + 1.425\ H_2SO_4(sln) = [0.475\ La_2(SO_4)_3 + 1.425\ H_2O](sln)$	−224.6 ± 0.9
(3) $0.95\ La(s) + 0.7125\ O_2(g) = 0.475\ La_2O_3(s)$	−851.8 ± 1.0
(4) $MnSO_4(s) + sln = MnSO_4(sln)$	−28.9 ± 0.8
(5) $Mn(s) + S(s) + 2\ O_2(g) = MnSO_4(s)$	−1065.3 ± 4.2
(6) $0.635\ H_2O_2(l) + [1.27\ FeSO_4 + 0.635\ H_2SO_4](sln) = [0.635\ Fe_2(SO_4)_3 + 1.27\ H_2O](sln)$	−203.63 ± 0.36
(7) $0.635\ H_2(g) + 0.635\ O_2(g) = 0.635\ H_2O_2(l)$	−121.4 ± 0.5
(8) $H_2SO_4(l) + sln = H_2SO_4(sln)$	−0.02 ± 0.02
(9) $H_2(g) + S(s) + 2\ O_2(g) = H_2SO_4(l)$	−873.7 ± 0.4
(10) $0.365\ H_2O(l) + sln = 0.365\ H_2O(sln)$	−0.22 ± 0.02
(11) $0.365\ H_2(g) + 0.1825\ O_2(g) = 0.365\ H_2O(l)$	−104.3 ± 0.02
(12) $0.95\ La(s) + Mn(s) + 1.53\ O_2(g) = La_{0.95}MnO_{3.06}(s)$	−1418.5 ± 6.8

Note: The solvent used is 0.150 dm^3 of 0.1 mol dm^{-3} $FeSO_4(NH_4)_2SO_4$ + 4.0 mol dm^{-3} of H_2SO_4. $FeSO_4(NH_4)_2SO_4$ is known as Mohr's salt and is a double salt of $FeSO_4$ and $(NH_4)_2SO_4$. As $FeSO_4$ is susceptible to oxidation, it is always stored as $FeSO_4(NH_4)_2SO_4$. The $(NH_4)_2SO_4$ part of this salt is not taking part in the reactions indicated in Tables 7 and 8. Therefore, it does not appear in the equations given for the thermochemical cycles in these tables.

Table 8
Reaction scheme for the standard molar enthalpy of formation of $Sm_{0.95}MnO_{3.09}(s)$ (sln = 0.150 dm^3 of 0.2 mol dm^{-3} $FeSO_4(NH_4)_2SO_4$ + 4.0 mol dm^{-3} of H_2SO_4) at 298.15 K. $\Delta H_{12} = -\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7 - \Delta H_8 - \Delta H_9 + \Delta H_{10} + \Delta H_{11}$.

Reaction	ΔH_m (kJ mol^{-1})
(1) $Sm_{0.95}MnO_{3.09}(s) + [1.33\ FeSO_4 + 3.09\ H_2SO_4](sln) = [0.475\ Sm_2(SO_4)_3 + MnSO_4 + 0.665\ Fe_2(SO_4)_3 + 3.09\ H_2O](sln)$	−309.1 ± 4.1
(2) $0.475\ Sm_2O_3(s) + 1.425\ H_2SO_4(sln) = [0.475\ Sm_2(SO_4)_3 + 1.425\ H_2O](sln)$	−213.5 ± 1.1
(3) $0.95\ Sm(s) + 0.7125\ O_2(g) = 0.475\ Sm_2O_3(s)$	−870.3 ± 4.0
(4) $MnSO_4(s) + sln = MnSO_4(sln)$	−30.4 ± 0.9
(5) $Mn(s) + S(s) + 2\ O_2(g) = MnSO_4(s)$	−1065.3 ± 4.2
(6) $0.665\ H_2O_2(l) + [1.33\ FeSO_4 + 0.665\ H_2SO_4](sln) = [0.665\ Fe_2(SO_4)_3 + 1.33\ H_2O](sln)$	−209.3 ± 0.3
(7) $0.665\ H_2(g) + 0.665\ O_2(g) = 0.665\ H_2O_2(l)$	−127.1 ± 0.6
(8) $H_2SO_4(l) + sln = H_2SO_4(sln)$	−0.34 ± 0.06
(9) $H_2(g) + S(s) + 2O_2(g) = H_2SO_4(l)$	−873.7 ± 0.4
(10) $0.335\ H_2O(l) + sln = 0.335\ H_2O(sln)$	−0.20 ± 0.01
(11) $0.335\ H_2(g) + 0.1675\ O_2(g) = 0.335\ H_2O(l)$	−92.9 ± 0.02
(12) $0.95\ Sm(s) + Mn(s) + 1.545\ O_2(g) = Sm_{0.95}MnO_{3.09}(s)$	−1425.9 ± 7.0

The enthalpy of formation of $LaMnO_3$ reported earlier investigators [1–4] varies between −1451.1 kJ mol^{-1} and −1421.5 kJ mol^{-1}. In these investigations, $LaMnO_3$ has been prepared by solid state method. Laberty et al. [2] have studied the energetics of rare earth manganese perovskites with dopants such as Sr and Ca at the A-site of the perovskite. They found that the substitution of the trivalent cation with the divalent one, causes the enthalpy of formation to become less negative as the divalent cation content is increased. The divalent cation content is directly related to the Mn^{4+} content. The value of enthalpy of formation of sample $La_{0.95}MnO_{3.05}(s)$, (−1418.5 ± 6.8 kJ mol^{-1}) obtained in this study, using a simple isoperibol calorimeter at 298 K is consistent with the observations of earlier investigators who have used high temperature calorimeter [2] (−1412.7 ± 6.04 kJ mol^{-1} for $La_{0.9}Sr_{0.1}MnO_3$).

There are no reported thermodynamic data on $SmMnO_3$ except phase equilibrium studies and thermogravimetric investigations of the Sm–Mn–O system by Kitayama et al. [19] at 1100 °C. As the Gibbs energy of formation of $SmMnO_3$ from the oxides is reported only at one temperature, i.e., 1100 °C, the enthalpy of formation could not be derived from this study. Therefore, we could not compare our results with any literature value for $Sm_{0.95}MnO_{3.09}$.

4. Conclusions

The structure and stoichiometry of $La_{0.95}MnO_{3+\delta}$ and $Sm_{0.95}MnO_{3+\delta}$ depends upon the method of preparation and annealing temperature. Using the sol–gel method, nanocrystalline $La_{0.95}MnO_{3+\delta}$ and $Sm_{0.95}MnO_{3+\delta}$ have been prepared in phase pure form at lower temperature. The enthalpies of formation of $La_{0.95}MnO_{3.06}$ and $Sm_{0.95}MnO_{3.09}$ at 298.15 K are found to be −1418.5 ± 6.8 kJ mol^{-1} and −1425.9 ± 7.0 kJ mol^{-1}, respectively, using a simple isoperibol calorimeter that works at room temperature.

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