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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 $\Phi = (\text{urea})/(La^{3+} + Mn^{2+})$. 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

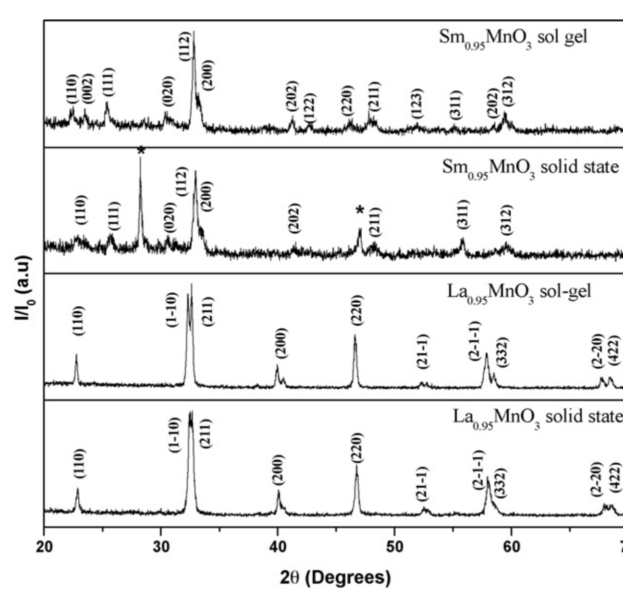

Fig. 1. XRD patterns of $La_{0.95}MnO_{3+\delta}$ and $Sm_{0.95}MnO_{3+\delta}$ prepared by solid state and sol–gel routes which were heated at 800 °C for 48 h (*Sm_2O_3).