THERMAL CHARACTERISATION OF THE NON-STOICHIOMETRY AND CATALYTIC ACTIVITY OF $Ba_x Ln_{1-x} CoO_3$ (Ln = La, Nd, Sm AND Dy) COMPOUNDS

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ABSTRACT

The compounds $Ba_x Ln_{1-x} CoO_3$ (Ln = La, Nd, Sm and Dy) were prepared by ceramic technique. They were characterised for oxygen non-stoichiometry using isothermal DTA under varying oxygen partial pressure and TG in air. Isothermal DTA was also employed to study the catalytic activity of the compounds towards CO oxidation. For a given compound, the oxygen deficiency increases with increasing temperature and decreasing oxygen partial pressure. For a given $Ba_x Ln_{1-x} CoO_3$ series, in general barium-rich compounds were more oxygen deficient. Isothermal DTA study of CO oxidation over $Ba_x La_{1-x} CoO_3$ compounds at 600 K suggested that the carbon monoxide takes up lattice-labile oxygen from the sample and is oxidised to CO_2, the percent CO conversion being higher for barium-rich samples.

INTRODUCTION

Perovskite-like compounds of the type $LnMO_3$ and $B_x Ln_{1-x} MO_3$ (Ln = rare earth, B = Ca, Sr, Ba, M = transition metal) have been extensively studied in the past for their solid state properties. Recent studies on their catalytic properties have revealed that they are potential oxidation–reduction catalysts. Pure and substituted rare earth cobaltites and manganites are promising in this regard. After Libby [1] suggested the use of $LaCoO_3$ in automobile pollution control, Sorenson et al. [2], Yao [3] and Parakash et al. [4] investigated the catalytic activity of rare earth cobaltites towards the oxidation of carbon monoxide and the catalytic activity was related to the spin state of cobalt ion. Thereafter, studies [5,6] on the stability of the perovskite phase in a reducing atmosphere by several workers indicate that the oxygen non-stoichiometry of the composition may play an important role in determining their catalytic activity.
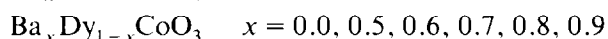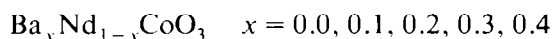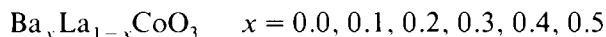
Generally, in oxides, the oxygen content can be quantitatively estimated

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by either chemical analysis or thermogravimetry in reducing atmospheres. In the present investigation, we have employed DTA and TG in normal as well as in isothermal mode to estimate the oxygen non-stoichiometry qualitatively in $Ba_xLn_{1-x}CoO_3$ (Ln = La, Nd, Sm and Dy) compounds. The results are presented here.

EXPERIMENTAL

Samples were prepared by the conventional ceramic technique. Appropriate homogeneous mixtures of the oxalates of the rare earth, barium and cobalt were decomposed at 900 K for 10 h, pelletised, and fired in air at 1500–1600 K for a few days. Formation of monophasic composition was checked by analysing the X-ray powder diffraction patterns recorded using CuK_α radiation ($\lambda = 1.5418$ Å). The following compositions were found to be monophasic

$Ba_xLa_{1-x}CoO_3$ $x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$
$Ba_xNd_{1-x}CoO_3$ $x = 0.0, 0.1, 0.2, 0.3, 0.4$
$Ba_xSm_{1-x}CoO_3$ $x = 0.0, 0.5, 0.6$
$Ba_xDy_{1-x}CoO_3$ $x = 0.0, 0.5, 0.6, 0.7, 0.8, 0.9$

Thermogravimetric analysis was carried out using a modified two pan balance [7], the advantage of which was that, even for large amounts of sample (a few grams), the balance sensitivity was very high (10 mg = 13 cm). When a sample (about 2 g) was heated to 1000 K in air, it showed a continuous mass loss with increase in temperature. At 1000 K in an isothermal condition, introduction of oxygen in the system showed a gain in mass due to oxygen uptake.

DTA in air did not show any phase transition up to 1000 K.

It is known that the cobaltites are generally oxygen deficient. To confirm and estimate the oxygen deficiency, oxidation of the sample was studied in the DTA cell. Under isothermal conditions, the enthalpy changes were recorded by varying the atmosphere around the sample (or by varying the oxygen partial pressure). The DTA runs were taken in two sets of experiments as follows.

(1) Air ($P_{O_2} = 0.2$ atm) replaced by oxygen ($P_{O_2} = 1$ atm).
(2) Ultrahigh pure (UHP) nitrogen ($P_{O_2} = 0$) replaced by oxygen ($P_{O_2} = 1$ atm).

The sample (400 mg) and the reference (alumina) were heated in platinum cups in the DTA cell in air to 1000 K. After maintaining the cell at this temperature for some time, oxygen was introduced into the cell. A sharp exothermic peak was observed due to oxygen uptake by the sample (oxidation). After completion of this reaction, introduction of air into the cell gave

a broad endothermic peak due to oxygen loss by the sample (reduction).

In another set of experiments, UHP nitrogen instead of air was used and exactly the same procedure was followed. In both sets of experiments, blank runs were taken with no sample in the holder. No exo- or endothermic peaks were observed.

It was also observed that the increase in temperature of the DTA cell increased the peak areas of the exotherms or endotherms. At 1000 K, enthalpy changes were sufficiently high and hence only these results are presented here.

The oxidation of carbon monoxide was studied in the DTA cell in an isothermal mode at lower temperatures at which catalytic reactions are generally carried out. Below 650 K, the compounds in N_2 do not lose oxygen to any appreciable extent. Hence oxidation of CO was studied at 600 K as follows.

The sample (400 mg) along with the reference was heated to 600 K in UHP N_2 in the DTA cell. After maintaining the cell at this temperature, CO was introduced. A sharp exothermic peak was observed due to oxidation of CO to CO_2. Carbon monoxide was then flushed out by UHP N_2. Introduction of oxygen at this stage gave a sharp exothermic peak due to the oxidation of the sample.

In all the DTA experiments, the gases were introduced in the DTA cell at a constant flow rate of about $1.0 \ 1 \ h^{-1}$.

As the samples had a very low surface area ($\sim 0.5 \ m^2 \ g^{-1}$), the time taken for the gases to enter the whole bulk of sample was very low and it could be assumed that the mass changes or enthalpy changes observed in TG and DTA, respectively, were of the whole sample.

RESULTS AND DISCUSSION

The TG in air for Ba–La and Ba–Nd cobaltites are shown in Figs. 1 and 2. The results show that, in both the systems, the mass loss increases with increasing barium content of the sample. At 1000 K, under isothermal conditions, introduction of oxygen produced an increase in mass, indicating that the earlier mass loss was due to oxygen leaving the lattice. Table 1 gives the percent mass gain in the sample as a result of introduction of oxygen in the system at 1000 K. Thus, for a particular sample at 1000 K, the composition is less oxygen deficient in a pure oxygen atmosphere than in air, indicating that the oxygen content of the sample is a function of oxygen partial pressure above it.

The composition of the sample can be written as $Ba_x Ln_{1-x} CoO_{3-\lambda}$ where λ is the oxygen deficiency. At higher temperatures, the sample can be oxidised or reduced by respectively increasing or decreasing the oxygen partial pressure in the DTA cell. As the enthalpies of oxidation and
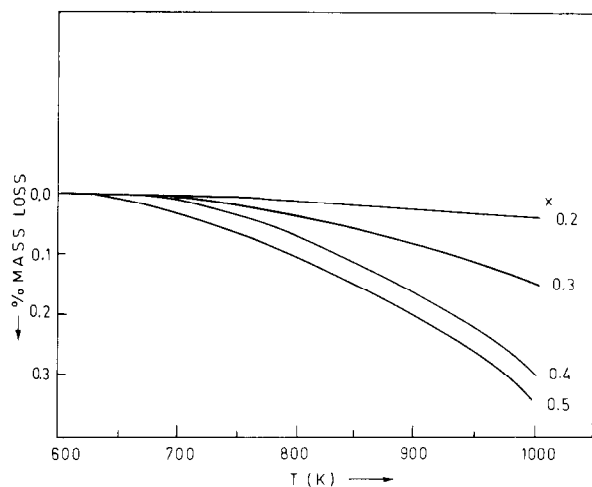
Fig. 1. Per cent mass loss versus temperature for the compositions $Ba_xLa_{1-x}CoO_3$.

reduction are sufficiently high, these reactions can be studied in the DTA cell.

The peak area of the exotherm is proportional to the oxygen taken up by the sample when P_{O_2} over it is increased and the peak area of the endotherm is proportional to the oxygen lost by it when P_{O_2} over it is decreased to the original value. The peak areas of both these reactions are nearly equal. As exothermic reactions were faster than the endothermic reactions, exothermic peaks only are given in Fig. 3 for various compositions. In the second set of experiments (Fig. 4), the change in the oxygen partial pressure is large (from 0.0 to 1.0 atm) and hence, for any sample, enthalpy changes are higher than
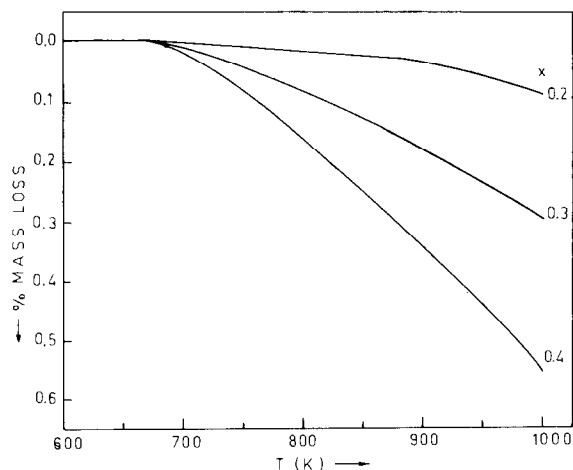

Fig. 2. Per cent mass loss versus temperature for the compositions $Ba_xNd_{1-x}CoO_3$.
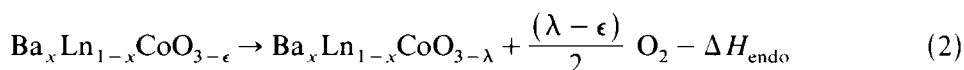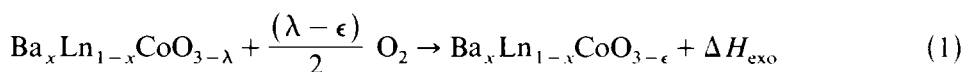
TABLE 1

Per cent mass gain for the compounds $Ba_xNd_{1-x}CoO_3$ at 1000 K when the atmosphere in the TG chamber is changed from air to oxygen

x	Mass gain (%)
0.2	0.045
0.3	0.057
0.4	0.083

those observed in the first set of experiments in which P_{O_2} changes only from 0.2 to 1.0.

The oxidation–reduction reactions occurring in the DTA cell can be written as

$$Ba_xLn_{1-x}CoO_{3-\lambda} + \frac{(\lambda - \epsilon)}{2}\, O_2 \rightarrow Ba_xLn_{1-x}CoO_{3-\epsilon} + \Delta H_{exo} \qquad (1)$$

$$Ba_xLn_{1-x}CoO_{3-\epsilon} \rightarrow Ba_xLn_{1-x}CoO_{3-\lambda} + \frac{(\lambda - \epsilon)}{2}\, O_2 - \Delta H_{endo} \qquad (2)$$

where $\epsilon < \lambda$ and the value of λ is higher in second set of experiments.

The area of the exo- or endothermic peak is proportional to the "labile" or exchangeable oxygen of the sample, $(\lambda - \epsilon)/2\ O_2$ from reactions (1) and (2). Also, results from both sets of experiments suggest that the amount of labile or exchangeable oxygen increases with decreasing oxygen partial
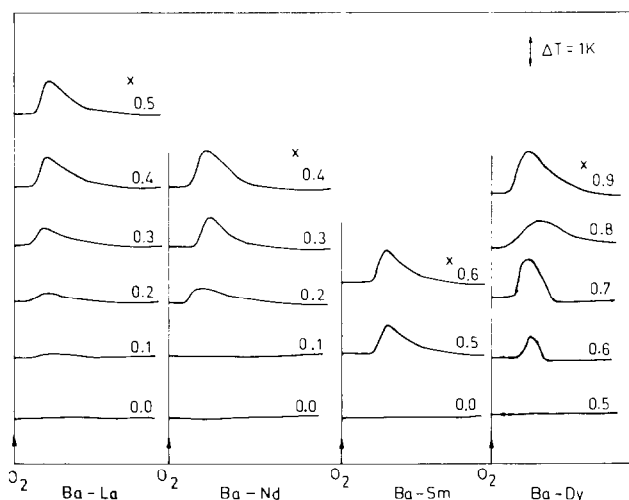

Fig. 3. Isothermal DTA exotherms for the compounds $Ba_xLn_{1-x}CoO_3$ (Ln = La, Nd, Sm and Dy) at 1000 K obtained by changing the atmosphere in the DTA cell from air to oxygen.

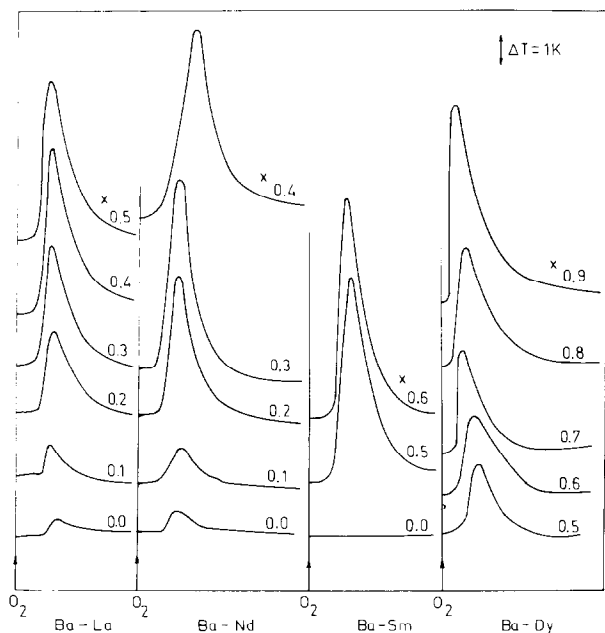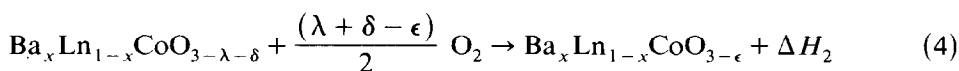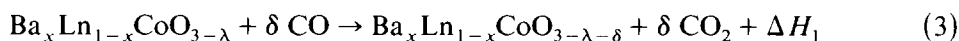Fig. 4. Isothermal DTA exotherms for the compounds $Ba_x Ln_{1-x} CoO_3$ (Ln = La, Nd, Sm and Dy) at 1000 K obtained by changing the atmosphere in the DTA cell from UHP nitrogen to oxygen.

pressure and also with increasing temperature. Comparison of results for different compositions in each series shows that the exchangeable oxygen content is higher in barium-rich samples.

It is interesting to check how the exchangeable oxygen of the sample is related to the catalytic activity of the sample towards CO oxidation. When the sample is heated to 600 K in UHP N_2, its composition is, say, $Ba_x Ln_{1-x} CoO_{3-\lambda}$. When N_2 is replaced by CO, CO is oxidised to CO_2 by taking up the lattice oxygen and the sample composition changes to $Ba_x Ln_{1-x} CoO_{3-\lambda-\delta}$. This sample is reoxidised to $Ba_x Ln_{1-x} CoO_{3-\lambda}$ when oxygen is introduced into the system. The reactions can be written as

$$Ba_x Ln_{1-x} CoO_{3-\lambda} + \delta \, CO \rightarrow Ba_x Ln_{1-x} CoO_{3-\lambda-\delta} + \delta \, CO_2 + \Delta H_1 \tag{3}$$

$$Ba_x Ln_{1-x} CoO_{3-\lambda-\delta} + \frac{(\lambda + \delta - \epsilon)}{2} \, O_2 \rightarrow Ba_x Ln_{1-x} CoO_{3-\epsilon} + \Delta H_2 \tag{4}$$

Thus, the enthalpy of the reaction (4), ΔH_2, is much higher than ΔH_{exo} of reaction (1), which is obviously due to the intermediate step of the introduction of CO in the system [reaction (3)]. In fact, the enthalpy ΔH_2 is equal to the sum of ΔH_1 and ΔH_{exo}. However, at 600 K, the ΔH_{exo} values of reaction (1) are very low (λ is very small) and hence, $\Delta H_2 \sim \Delta H_1$. In Fig. 5, the exotherms of reaction (4) are shown for various compositions in Ba–La cobaltites. The values of the enthalpy changes (ΔH_2) for various composi-
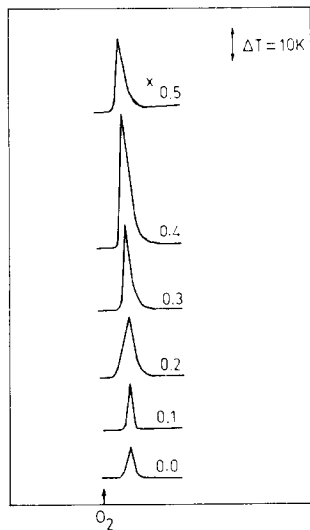
Fig. 5. Isothermal DTA exotherms for the compounds $Ba_xLa_{1-x}CoO_3$ at 600 K.

tions, x, are in the order $0.5 \sim 0.4 > 0.3 > 0.2 > 0.1 > 0.0$.

Our studies on the catalytic activity of these compounds towards CO oxidation [8] show that the activity follows exactly the same trend as that of the value of ΔH_2. Thus, the oxidation of CO in the DTA cell studied here provides a rapid and relatively convenient method for checking the catalytic activity of these materials towards CO oxidation.

The oxygen-deficient nature of these materials is also reflected in their electrical and magnetic properties [9–11]. Incorporation of divalent barium in the $LnCoO_3$ does not produce tetravalent cobalt only, but also the oxygen vacancies, giving an overall composition of $Ba_xLn_{1-x}Co^{3+}_{(1-x+y)}Co^{4+}_{(x-y)}O_{(3-y/2)}$.

In conclusion, the results suggest that the composition of these compounds is dependent on the surrounding oxygen partial pressure and also on the temperature. The study of the oxidation of CO over the sample in the DTA cell presents a rapid method of checking the catalytic activity of the sample towards CO oxidation. In elucidation of the mechanism of catalytic activity of these compounds, due consideration should be given to the role of oxygen non-stoichiometry of the composition, which is highly dependent on the temperature and the atmosphere inside the catalytic reactor.

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