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Electrical, magnetic and catalytic oxidation studies on $LaMn_{1-X}Co_XO_3$ system

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Lanthanum manganates and cobaltates and their intermediate compositions $LaMn_{1-X}Co_XO_3$ (x = 0.0, 0.3, 0.5, 0.7 and 1.0) with a perovskite structure have been synthesized by co-precipitation precursor technique. These compounds show phase transitions from semi-conductor to semi-metallic in the range of 570-630 K and also considerable increase in activity of carbon monoxide oxidation to carbon dioxide. An attempt has been made to understand the effect of B-site substitution in the lattice of $LaMnO_3$ and their correlation with the solid-state properties.

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Perovskites (ABO_3) exhibit a variety of applications in electronics, magnetic materials and as catalysts[1]. Some $LaBO_3$ oxides (B = a first row transition metal) are found to be promising catalysts for the total oxidation of carbon monoxide on account of their better activity and thermal stability as compared to individual oxides[2-5]. In addition to their activities, they are not significantly affected by poison such as Pb and S present in the automotive exhaust gases, thus making these materials promising as anticontamination catalysts. The catalytic activity of these perovskite oxides can be suitably modified by incorporating different metal ions in the lattice to improve the quality of the materials. The oxidation of CO with the aim of reducing air pollutant is obviously an important consideration in terms of automobile and industrial pollution control. Several investigators[6,7] have studied the solid state and catalytic activity of CO oxidation over $LaMnO_3$, $LaCoO_3$ and intermediate compounds. Their studies have shown that the non-noble metal containing catalysts such as cobalt and manganese are chemically active species for CO oxidation. In the present investigation an attempt has been made to understand the effect of B-site substitution by cobalt in the lattice of $LaMnO_3$ and to show the comparative catalytic activity of manganates with various cationic compositions prepared by co-precipitation precursor technique in the oxidation of CO and their correlation with the spectroscopic and solid-state properties.

Materials and Methods

The perovskite type compositions of $LaMn_{1-X}Co_XO_3$ were synthesized by co-precipitation precursor technique as discussed earlier[6,8,9]. Stoichiometric quantities of La_2O_3, Mn/Co nitrates (AR) were dissolved in minimum quantity of 1:1 nitric acid and distill water respectively. Aqueous solutions were mixed and precipitated using 5% sodium hydroxide solution. The precipitate obtained was digested on a steam bath and the resultant precipitated hydroxide mixture was subjected to oxidation using 30% H_2O_2. The precipitate was then washed, filtered and dried in an oven at 353 K. The dried precipitate was homogenized well in an agate mortar and further heated in air for 10-12 hrs at 1073 K.

The compositions prepared were characterized by X-ray powder diffraction technique with Philips X-ray diffractometer (PW 1820) and Rigaku Miniflex instruments, using Cu Kα, filtered through Ni absorber. FTIR spectra were recorded on a Shimadzu FTIR instrument (model 8101A). The sodium contamination in the perovskites prepared by co-precipitation method using sodium hydroxide was found by employing atomic absorption spectroscopy. The total BET surface areas were measured using BET nitrogen adsorption method (QUANTACHROME NOVA 1200 version 3.70). Electrical conductivity measurements were carried out by two-probe conductivity unit in the temperature range of room temperature to 873 K. The magnetic susceptibility 'χ_g' in air of the perovskites were determined by Gouy method at room temperature employing a field of the order of 10,000 gauss and using $Hg[Co(SCN)_4]$ as standard material. ESR study was carried out for the perovskites containing paramagnetic species and for the identification of the catalytically active species for the reaction. The ESR spectra were recorded at the X-band on a Varian E-112 spectrophotometer at liquid nitrogen temperature. The sample was mounted on a quartz tube and TCNE was used as a field calibrant taking its g-value as 2.00277. The saturation magnetization was studied considering the hysteresis behaviour. These measurements were done on selected magnetic samples, using a high field hysteresis loop tracer. The saturation magnetization values, σs in emu/g, of some magnetic perovskite samples were measured.

CO oxidation was studied using oxygen in nitrogen with a continuous flow, fixed bed glass reactor by placing around 1g of powdered catalyst in between glass wool plugs. The catalytic activity was determined using a feed gas composition of 5% CO and 5% O_2 in nitrogen for CO oxidation. The individual gas flow rates were controlled using flow meters and precision needle valves. The feed gases and the products were analyzed employing an online gas chromatograph with molecular sieve 13X and Porapak Q columns. H_2 was used as a carrier gas. The CO was prepared in the laboratory by standard procedure, further purified by passing through alkali and molecular sieve traps[10]. The oxygen and nitrogen gases were used from pure commercial cylinders.

Results and Discussion

The compositions prepared were characterized by recording X-ray powder diffractograms. The d_{hkl} and 2θ values obtained were compared with the values reported in the literature (JCPDS data file) and found to be in good agreement. Since the d_{hkl} values of the intermediate compositions are not reported in the literature, the values were compared with the end compositions. Fig. 1 shows XRD pattern for the representative samples.

The sodium contamination was estimated using an AAS and was found to be in the range of 0.3-0.5% by weight. Surface areas obtained by BET nitrogen adsorption method were found to be in the range of 5.4-12.6 m^2/g for these compositions.

The perovskite structure is characterized by IR spectra[12] in the region 1000-300 cm^{-1}. In the IR spectra of perovskites, two absorption bands were observed in the 700-390 cm^{-1} region corresponding to the stretching vibration of metal-oxygen bond. The lower frequency band has been assigned to a deformation mode of BO_6 (B = Mn or Co) octahedra, i.e., the B-O-B bond angles of the perovskite structure. The frequency of these bands has been related to the strength of metal-oxygen covalency. It is observed that as the substitution of Co^{3+} increases in $LaMnO_3$, the strong absorption peak observed at 606 cm^{-1} gets gradually broadened for composition from x = 0.0-0.7 and shifts towards lower frequency. The FTIR spectra for x = 0-x ≤ 0.5 showed similar pattern, whereas for x > 0.5 distorted shouldered peaks were seen, which may be due to slight structural symmetry change. The compositions of x ≤ 0.5 have a higher structural symmetry than x > 0.5. This is synonymous with the reports of Yang *et al.*[11]. In the case of $LaCoO_3$, a broad absorption with peaks at 600 and 570cm^{-1} were observed which is in agreement with the literature[12]. The absorption band at 606 cm^{-1} shifts towards lower wave number value as x increases which is due to e_g electrons in the antibonding orbitals. Therefore bond order would decrease with the increase in the number of e_g electrons. This accounts for the observed decrease in the stretching frequency of $LaMnO_3$ on substitution with Co.

Electrical resistivities of different perovskites were measured using two-probe method from room temperature to 873 K. It was observed that resistivity decreases with increase in temperature for all the compositions. For $LaMnO_3$, a decrease in the range from room temperature to 415 K, followed by a sharp jump of the resistivity at around 570 K and for further rise of temperature beyond 600 K, very small change in the resistivity was observed. This sharp change in

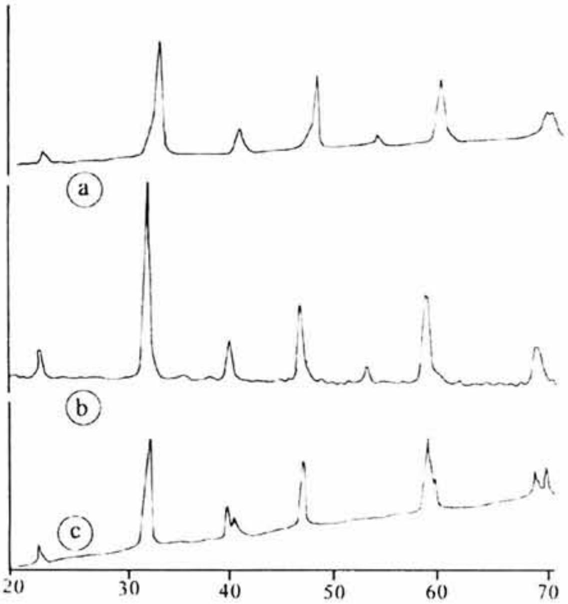

Fig. 1—XRD pattern for representative samples (a) $LaMnO_3$, (b) $LaMn_{0.5}Co_{0.5}O_3$ and (c) $LaCoO_3$.

the resistivity is an indication of a broad phase transition occurring in the range of 560-630 K. A broad higher order semi-conductor to semi-metallic transition between approximately 560 and 630 K has been observed for $LaCoO_3$, in agreement with Rao[13] and Thornton *et al* [14]. The intermediate compositions showed similar trend of resistivity with broad transitions. However, it was noticed that the transitions for the intermediates occurred at higher temperatures than for the end compositions. $LaMn_{0.7}Co_{0.3}O_3$ showed higher resistivity than others. The measurements were repeated on the same set of samples twice and observed same trends of resistivity behaviour.

The influence on the structure of $LaMnO_3$, however is the overall amount of Mn^{4+} ions. The cooperative ordering of the Jahn-Teller distorted $Mn^{3+}O_6$ octahedra leads to the orthorhombic structure of $LaMnO_3$[15]. This ordering is destroyed by an increase in the overall amount of Mn^{4+} on the room temperature structure of $LaMnO_3$, due to an increase in the oxygen content. Thornton *et al.*[14] explained a broad semi-conductor to metal transition in $LaCoO_3$ in the range of 520-750 K by the stabilization of an intermediate spin state of $CO^{(III)}$ ($t_{2g}^5\ e_g{*}^1$) that is associated with a smooth transition from localized e_g to itinerant σ^* electrons at trivalent cobalt ions. Thus a long range ordering of the spin states occurs in addition to charge transfer between the spin states to form $Co^{(II)}$ and $Co^{(IV)}$ species. They also observed a continuous decrease in the rhombohedral angle as a function of temperature by neutron diffraction. Norby *et al.*[16] observed the orthorhombic $LaMnO_3$ to cubic transformation at around 600 K. $LaMnO_{3+\delta}$ can crystallize with either orthorhombic or rhombohedral symmetry depending on the value of δ. At higher value of δ, $LaMnO_{3+\delta}$ crystallizes with rhombohedral symmetry. The rhombohedral $LaMnO_{3+\delta}$ is expected to show more ion pairs of Mn^{3+}- Mn^{4+}, but because of Na in the lattice will reduce Mn^{4+} ions showing overall higher resistivity than $LaCoO_3$, which is slightly oxygen deficient compound[6]. This gives an indication that the observed semiconductor to semi-metallic transition might have accompanied by structural symmetry transformation.

The magnetic susceptibility of different samples was determined by Gouy balance at room temperature using field strength of 10,000 gauss. Since $LaMnO_3$ and other intermediate compositions are antiferromagnetic at room temperature, the χ_g value was measured only for $LaCoO_3$. $LaCoO_3$ is paramagnetic, with χ_g value of 3×10^{-5} emu/g and μ_{eff} value of 3.4 B.M. The observed saturation magnetization values of different perovskites are presented in Table 1. It is observed that the Co^{3+} ions in the intermediate compositions do not lie in the low spin state (S = 0). They have magnetic moments much less than that of the Mn^{3+} ions[15]. Topfer[17] reported that $LaMnO_3$ is able to display a large range of non-stoichiometry in both the La/Mn ratio and the oxygen content. At higher oxygen activity, oxygen excess $LaMnO_{3+\delta}$ accommodates the excess oxygen by creating vacancies. In compounds La/Mn $\neq$ 1, the δ = 0 composition has vacancies on the oxygen array as well as the cation-deficient array since the structure accommodates vacancies more readily than interstitial atoms. In the rhombohedral structure of $LaMnO_{3+\delta}$, as the Mn is substituted with Co^{3+} ions, the Mn^{4+}/Mn^{3+} ions ratio decreases. Antiferromagnetic behaviour of $LaMnO_3$, which is attributed to the clusters sufficiently rich in Mn^{4+} ions becomes paramagnetic for $LaCoO_3$, thus lowering the net magnetization of the system as seen in the Table 1.

While these compounds did not show any ESR spectra at room temperature, at liquid nitrogen, they showed broad spectra. ESR data of different perovskites at liquid nitrogen temperature are presented in Table 1. For heavier atoms like La^{3+}, the spin–orbit coupling is strongly coupled to lattice vibrations and spin relaxation time, therefore, it is very small at high temperatures. This means that ESR spectra are too broad to be detected even at room temperature. Therefore, the above compounds do not show any spectra at room temperature but show broad spectra at liquid nitrogen temperature. The *g*-value of $LaMn_{1-X}Co_XO_3$ system is found to increase with increase in 'x' value. A very weak ESR signal with broad line width was observed only at liquid nitrogen temperature for $LaMn_{1-X}Co_XO_3$ system, giving an

Table 1—Saturation magnetization and ESR data of different perovskites

Catalysts	Saturation magnetization at 300 K (emu /g)	g-Value (80 K)	Line width (gauss)
$LaMnO_3$	13.9	2.9	Very broad signal
$LaMn_{0.7}Co_{0.3}O_3$	9.5	4.5	2020
$LaMn_{0.5}Co_{0.5}O_3$	8.8	3.0	1960
$LaMn_{0.3}Co_{0.7}O_3$	8.7	5.9	1420
$LaCoO_3$	-	3.7	940

indication that Mn^{3+}, Mn^{4+} and Co^{3+} ions are ESR inactive.

The temperature dependence of CO conversion studies for different compositions of $LaMn_{1-X}Co_XO_3$ is shown in Fig. 2. Incorporation of cobalt in the lattice of $LaMnO_3$ showed a significant change in the catalytic activity for CO oxidation. For $LaMnO_3$, the induction temperature is high as compared to other compounds. $LaCoO_3$ showed a rapid CO conversion between 373-398 K and around 80% conversion was observed at 398 K. The catalytic activity of rare earth cobaltates for the oxidation of CO to CO_2 can be related to spin and valence state of Cobalt[17]. $LaCoO_3$ shows the presence of both high spin and low spin trivalent Co ions. Magnetic susceptibility studies showed that $LaCoO_3$ has low spin $Co^{(III)}$ t_{2g}^{6} e_g^{0} at a particular temperature range (Tt) up to 398 K. Above that, electron transfer from high spin Co^{3+} to low spin $Co^{(III)}$ produces intermediate spin $Co^{(IV)}$ t_{2g}^{4} e_g^{1} ions and low-spin $Co^{(II)}$ t_{2g}^{6} e_g^{1} states[16]. This is followed by the onset of a short range ordering around 398 K, accompanied with simultaneous increase in Co^{3+} concentration and cation-anion movements. It is possible that Co^{3+}(high spin) sites facilitate the adsorption of CO in the presence of other Co states, particularly $Co^{(III)}$ low spin. In the $LaMn_{1-X}Co_XO_3$ series, when Mn is partly substituted by Co^{3+} ions, the activity sharply increases. Mn^{3+} ions being a high spin t_{2g}^{3} e_g^{1}, exhibit a localized behavior of *d*-electrons having lower catalytic activity. Therefore with the decrease of Mn/Co ratio, the concentration of high spin Mn^{3+} decreases, resulting in gradual increase of the catalytic activity. It may be noted that the electronic configuration may not be the only criteria for the activity. Also, other factors such as surface area, electrical resistivity, bond strength among others also influence the activity. It is observed that in spite of low surface area, $LaCoO_3$ showed higher activity. It is known that $LaCoO_{3-\delta}$ is oxygen deficient giving rise to Co^{2+} ions for the charge neutrality. Since these perovskites were prepared by co-precipitation precursor method using NaOH, the total removal of sodium is difficult; atomic absorption gave around 0.4% sodium. This means that incorporation of Na in $LaCoO_3$ lattice might have converted $Co^{3+} \rightarrow Co^{2+}$, thus destabilizing the Co-O-Co bond, favouring easy release of lattice oxygen to CO, giving enhanced activity. Also $LaCoO_3$ showed lower electrical resistivity indicating more free electrons than other compounds favouring more CO adsorption. Whereas $LaMnO_{3+\delta}$ is oxygen efficient, giving rise to Mn^{4+} ions for charge neutrality and sodium in the lattice might have converted $Mn^{4+} \rightarrow Mn^{3+}$, making Mn-O-Mn bond more stable. As a result more energy is required to release the lattice oxygen and therefore lower activity than $LaCoO_3$ is observed. The small amount of cobalt acts as a p-type dope in $LaMnO_3$ by the formation of Mn^{4+} and Co^{2+} ions. Therefore Co substituted in $LaMnO_3$ gives rise to more Mn^{3+}-Mn^{4+} ion pairs, favouring more CO adsorption and increased catalytic activity than $LaMnO_3$.

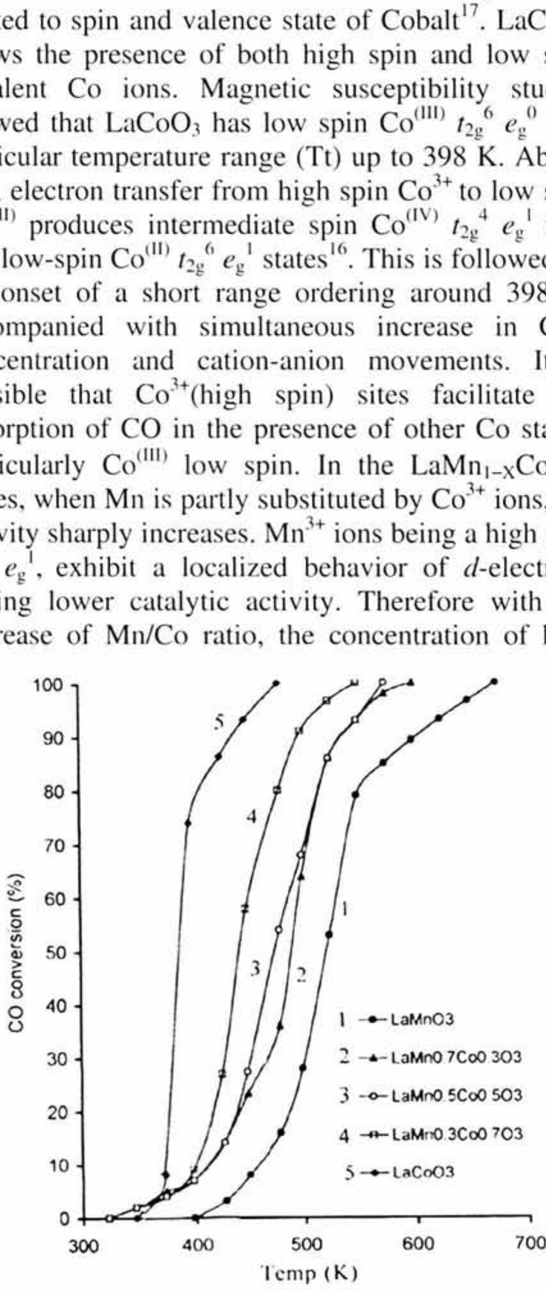

Fig. 2—CO conversion as a function of catalyst temperature.

The catalytic activity and the kinetic measurements of different compositions were carried out. Linear plots were observed for fractional conversion of CO (XCO) versus W/FCO at different temperatures, where W is the mass of catalyst and FCO is the number of moles of CO flowing per hour. The kinetic parameters were calculated from the Arrhenius plots and are summarized in Table 2. It is observed that the rate of reaction increases with the cobalt substitution in the B-site of $LaMnO_3$ from 1.0456×10^{17} to 7.7457×10^{17} molecules/m^2.s. The percentage

Table 2—Kinetic parameters of CO oxidation over $LaMn_{1-X}Co_XO_3$ catalysts at 393 K

Catalysts	Surface area (m^2/g)	Rate (Molecules/m^2.s)	E_a (Kcal/mole)
$LaMnO_3$	10.1	1.04×10^{17}	10.36
$LaMn_{0.7}Co_{0.3}O_3$	9.0	2.47×10^{17}	9.77
$LaMn_{0.5}Co_{0.5}O_3$	12.6	2.52×10^{17}	9.82
$LaMn_{0.3}Co_{0.7}O_3$	7.9	5.46×10^{17}	9.63
$LaCoO_3$	5.4	7.74×10^{17}	9.28

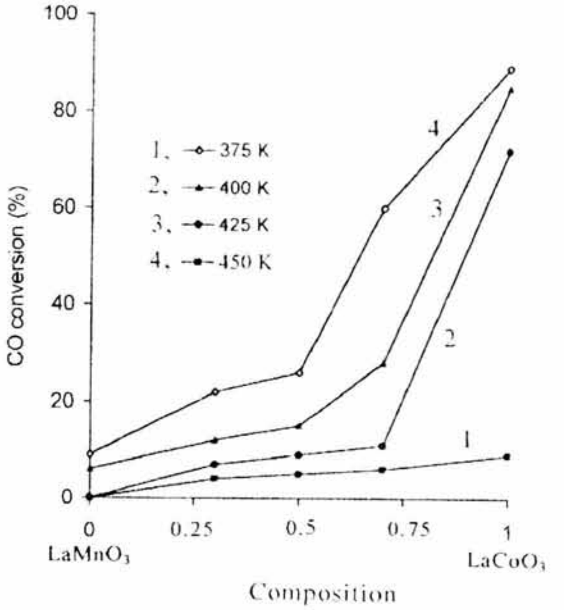

Fig. 3—Percentage conversion as a function of catalyst compositions for the $LaMn_{1-X}Co_XO_3$ system.

conversion as a function of catalyst compositions (x = 0.0-1.0) for the $LaMn_{1-X}Co_XO_3$ system is shown in Fig. 3 It is seen that $LaCoO_3$ shows significantly higher conversion at all the temperatures as compared to others compositions.

Conclusion

A significant rise in the catalytic activity is observed by B–site substitution of Co^{3+} in $LaMnO_3$ perovskite. $LaCoO_3$ shows higher activity in this series for CO oxidation while $LaMnO_3$ shows the least. The intermediate compositions show in between catalytic activity. Phase transitions from semi-conductor to semi-metallic are observed in the range of 560-630 K for all these compounds. $LaMnO_3$ show antiferromagnetic behaviour and with Co^{3+} substitution a decrease in saturation magnetization is observed. These compounds are ESR inactive at room temperature but show broad peaks at liquid nitrogen temperature due to spin-orbit coupling.

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