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Gas sensing behavior of modified $LaMnO_3$ ceramic

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The preparation of $LaMnO_3$ and $La_{1-x}Sr_xMnO_3$ (x in the range of 0.1-0.2) powders by polymerizable complex route and the synthesis of $La_{0.8}Sr_{0.2}MnO_3$:Pd (1 wt. %) gas sensors by chemical wet method are described in some details. Thick films of all samples were measured for their sensitivities in the temperature range 100-350 ^oC against the reducing gases like CO, NH_3, H_2 and LPG. $La_{0.8}Sr_{0.2}MnO_3$ has shown good sensitivity for CO gas at about 270 ^oC. Incorporation of palladium further improved the selectivity and sensitivity to CO gas by reduction of operating temperature from 270 ^oC to 200 ^oC. 1 wt.% Pd incorporated in $La_{0.8}Sr_{0.2}MnO_3$ was able to detect up to 50 ppm CO in air at an operating temperature of 200 ^oC. The improved sensitivity of the perovskite compound is attributed to the finer and homogeneous powders obtained by adopting polymerizable complex route as well as incorporation of noble metal.

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1. Introduction

Chemical sensors are being widely deployed for environmental monitoring, industrial hazard detection and sensing of chemical warfare agents. The development of reliable and selective solid-state gas sensors has great importance both in the field of atmospheric pollution and in the emission control from combustion plants. Recently, many efforts have been aimed to improve the gas sensor performances. Improved selectivity has been obtained by addition of catalysts and/or dopants, [1] while significant improvement of performance can be achieved by decreasing the particle size down to nanometre scale, thus obtaining an increased specific surface area [2]. Perovskite based materials are widely studied for technical microelectronic applications. ABO_3-type perovskite oxides (A = rare earth element with or without its partial substitution by alkaline earth element, and B = transition element such as Co, Mn, Ni, Fe, etc., with or without its partial substitution by other transition elements) have high potential for their use as catalysts in a number of catalytic reactions [3-7]. Recently, lanthanum-based perovskite have attracted much attention due to their electrical, magnetic, structural and catalytic properties [8].

The perovskite-type oxide solid solutions La_{1-x} Sr_x M $O_{3-\delta}$ (M = Cr, Mn, Fe, Co,) have been extensively studied due to their potential application as an air electrode in high-temperature oxide fuel cells, chemical sensor elements and electrodes for magnetohydrodynamic (MHD) generators, because some of them show high catalytic activity. Several useful properties of these perovskite-type oxides such as electrical conductivity and electron emission are the result of their nonstoichiometry and electronic structure.

Lanthanum magnetite ($LaMnO_3$) is a p-type perovskite oxide and shows reversible oxidation–reduction behavior. It is an insulator in all temperatures and exhibits antiferromagnetic transition with Neel temperature (T_N) at around 140K [9]. $LaMnO_3$ suitably doped with alkaline and rare earth element is generally used for the cathode in fuel cells. Duan *et. al* has investigated the compound $La_{0.7}Sr_{0.3}MnO_3$ for its magnetic properties [10]. Strontium oxide doped in $LaMnO_3$ is a mixed transition metal oxide with catalytic properties for several industrial applications. The substitution of divalent atoms in place of trivalent La with chemical formula $La_{1-x}D_xMnO_3$ (D = Sr, Ca and Pb), introduces the mixed valency of Mn^{3+} and Mn^{4+}. It has been reported that these divalent substituted compounds when doped to $LaMnO_3$ leads to increased electronic disorder and the change in an oxidation state of Mn.

This paper is aimed to determine the sensing properties of $La_{1-x}Sr_xMnO_3$ (x in the range of 0-0.2). A polymerizable complex (PC) method was for synthesis of the samples in order to get the nanosized $La_{1-x}Sr_xMnO_3$. It has been reported that, by better mixing and a good distribution of cations (La^{3+}, Sr^{2+} Mn^{3+} and Mn^{4+}) in the solutions were achieved by the PC method [11]. The materials were studied for their gas sensing behavior for reducing gases like CO, NH_3, LPG and H_2 at different temperatures.

2. Experimental

2.1 Synthesis of $La_{1-x}Sr_xMnO_3$ (x=0, 0.1, 0.15 and 0.2) powders

The $La_{1-x}Sr_xMnO_3$ compounds were prepared for x = 0, 0.1, 1.5 and 0.2 by nitrate route. At 80 ^oC, a calculated quantity of citric acid (CA) was firstly dissolved in a small quantity of deionized water followed by the addition of stoichiometric ratio of lanthanum nitrate, strontium nitrate and manganese nitrate. The mixture was magnetically stirred at 60 ^oC for 3 hr in order to obtain stable metal-CA complexes. After stirring, appropriate amount of ethylene glycol (EG) was added to this solution. The solution so obtained was continuously stirred on a hot

plate with a magnetic stirrer at 90 ^oC for 7 hr to remove the excess of water. This facilitates the polyesterification between CA and EG leading into formation of a resin like mass. The polymeric resin was decomposed by heating at 350 ^oC. The decomposed resin was treated in a mantle heater at 400-450 ^oC over 3 hr in order evaporate highly combustible species and induce charring. The resulting ash was slightly ground in to powder and calcined at 700 ^oC for 6 hr.

2.2 Pd incorporation over $La_{0.8}Sr_{0.2}MnO_3$ compound

Appropriate weights of palladium nitrate were dissolved in distilled water and then appropriate weight of $La_{0.8}Sr_{0.2}MnO_3$ (obtained by polymerizable complex route) was added to this solution. This solution was the stirred on magnetic stirrer. After several hours, the sample was slowly heated to dryness with stirring and then heated at 450^0C for 5 hr in air.

2.3 Gas sensing measurements

Above prepared powders mixed with an organic binder. The obtained fresh pastes were applied on to alumina tube substrate provided with two gold electrodes, heating coil fixed in the tube and leads. On drying, they were sintered at 550 ^oC for 2 hr.

Gas sensing properties were investigated at various operating temperatures from 100 to 350^0C. The experiments were performed with four test gases: CO, NH_3, H_2 and LPG (all 100% pure). Conductance measurements were performed in a sealed test chamber with different test gases in dry air, at a flow rate of 0.5 l/min. The sensitivity, *S*, is defined as the ratio:

$$S = \Delta R/R_{air}$$
$$\text{but, } \Delta R = R_{air} - R_{gas}$$

where R_{air} and R_{gas} are the sensor resistances in air and in presence of the test gas, respectively.

3. Results and discussion

3.1 Gas sensing characteristics of $La_{1-x}Sr_xMnO_3$

In the sensitivity measurement, the sensor elements were exposed to reducing gases like (all 100% concentrated) CO, NH_3, H_2 and LPG. The sensor elements were maintained at different temperatures but gases were introduced in a test chamber at room temperature. On exposure to the reducing gases, voltage across the sensor element was increased indicating a p-type semiconducting behavior.

The sensitivity of $La_{1-x}Sr_xMnO_3$ (x=0, 0.1, 1.5 and 0.2) sensors to CO. NH_3, H_2 and LPG gases were measured at different temperatures and results are presented in figures 1-4. Fig. 1 shows sensitivity of pure $LaMnO_3$ to various gases in the range of temperature 100-350^0C. It shows that, the sensitivity increases in the order of LPG<H_2<NH_3<CO. At 320 ^oC sensitivity of element to CO is slightly high than the NH_3. Fig. 2 shows the sensitivity of $La_{0.9}Sr_{0.1}MnO_3$ as a function of operating temperature. The sensing characteristic indicates that, with a small quantity of strontium, sensitivity of the element is increased for CO at 300 ^oC and that for NH_3 is decreased. Sensitivity of $La_{0.85}Sr_{0.15}MnO_3$ as shown in

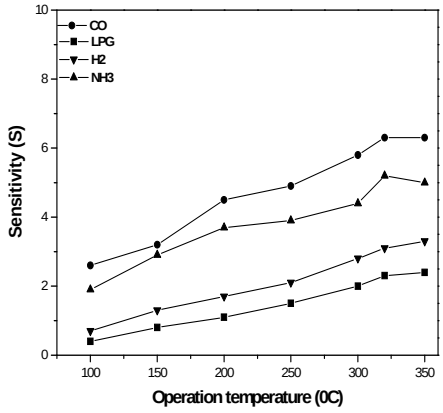

Fig. 1. Gas sensing characteristics of $LaMnO_3$.

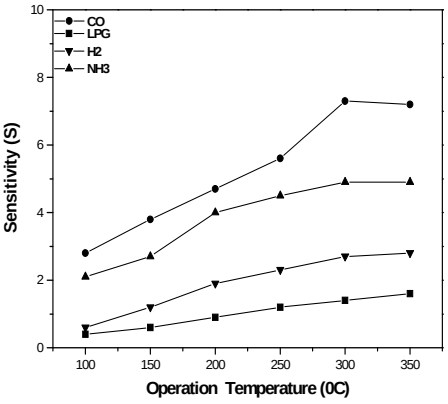

Fig. 2. Gas sensing characteristics of $La_{0.9}Sr_{0.1}MnO_3$.

Fig. 3, does not show any remarkable change in sensitivity to CO gas but that of NH_3 is dropped. Fig. 4 depicts the sensor response of $La_{0.8}Sr_{0.2}MnO_3$ as a function of temperature. It can bee seen from figure that, the element show a high sensitivity to CO at 270 ^oC. However, the sensitivity to NH_3, H_2 and LPG decreases. It reveals that though the material senses all gases at higher temperatures but the sensitivity at 270 ^oC for CO is much higher as compared to NH_3, H_2 and LPG. It is clear from Fig. 4 for $La_{0.8}Sr_{0.2}MnO_3$ that the sensitivity for CO has reached saturation at around 270 ^oC. The improved sensing characteristics are possibly due to increased conductivity by creation of sufficient number of active sites on doping for divalent Sr ions (x = 0.2) in $LaMnO_3$. The addition of some catalytically active compounds is

known to improve the gas sensing property [12] and is therefore, expected that the gas sensing properties of $La_{0.8}Sr_{0.2}MnO_3$ could also improve by such considerations. With the intention of increasing the sensitivity of $La_{0.8}Sr_{0.2}MnO_3$ it was further modified by impregnation of palladium (Pd).

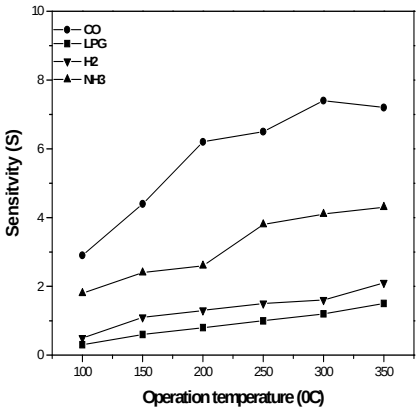

Fig. 3. Gas sensing characteristics of $La_{0.85}Sr_{0.15}MnO_3$.

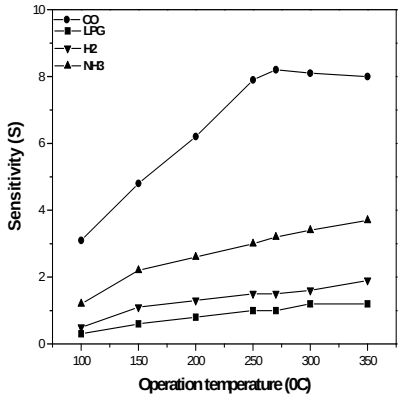

Fig. 4. Gas sensing characteristics of $La_{0.8}Sr_{0.2}MnO_3$.

3.2 Effect of Pd impregnation

In the present investigation, $La_{0.8}Sr_{0.2}MnO_3$ showed better sensitivity better sensitivity among all the samples therefore further studies were carried on this material. To enhance the sensitivity and selectivity as well as to reduce the operating temperature, different weight % of Pd have been incorporated into the $La_{0.8}Sr_{0.2}MnO_3$ sensor. A chemical wet impregnation method was employed for incorporation of Pd in $La_{0.8}Sr_{0.2}MnO_3$ and the gas sensing properties of each composition to CO, NH_3, H_2 and LPG gases were studied. The sensitivity of Pd impregnated $La_{0.8}Sr_{0.2}MnO_3$ was tested against operation temperature in the range of 100-240 ^oC. Fig. 5 shows the sensitivity of the element $La_{0.8}Sr_{0.2}MnO_3$:Pd (0.5 wt.%) as a function of operating temperature. It can bee seen from the figure that, with incorporation of Pd, the operating temperature is reduced to about 250 ^oC and at this temperature sensitivity to CO gas is maximum. But sensitivity to LPG and H_2 is almost negligible and that for NH_3 is one third of the CO.

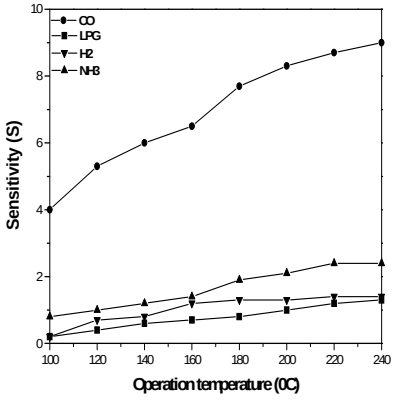

Fig. 5. Gas sensing characteristics of $La_{0.8}Sr_{0.2}MnO_3$:Pd (0.5 wt.%).

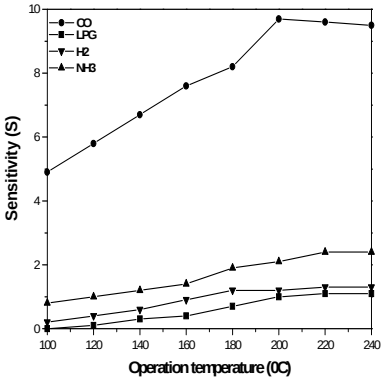

Fig. 6. Gas sensing characteristics of $La_{0.8}Sr_{0.2}MnO_3$:Pd (1 wt.%).

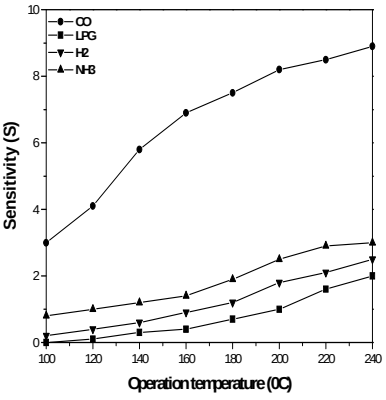

Fig. 7. Gas sensing characteristics of $La_{0.8}Sr_{0.2}MnO_3$:Pd (1.5 wt.%).

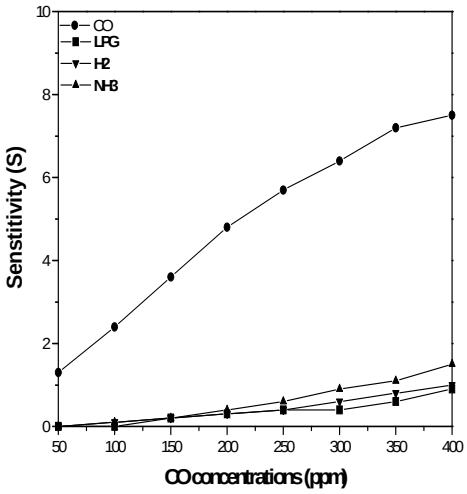

Fig. 8. Sensitivity vs. CO concentration in air at 200^{0}C for the sample $La_{0.8}Sr_{0.2}MnO_3$:Pd (1 wt.%).

Fig. 6 depicts an excellent sensor response by $La_{0.8}Sr_{0.2}MnO_3$:Pd (1 wt. %) to CO at 200^{0}C whereas the sensitivity to other reducing gases falls below 30%. Fig. 7 shows that, for sensor $La_{0.8}Sr_{0.2}MnO_3$:Pd (1.5 wt. %) the sensitivity to CO gas is decreased at lower temperature as compared to $La_{0.8}Sr_{0.2}MnO_3$:Pd (1 wt. %). Since 1 wt. % Pd addition is effective for CO detection, the sensitivity of this element as a function of CO concentration in air is analyzed. Fig. 8 shows the sensor response of $La_{0.8}Sr_{0.2}MnO_3$:Pd (1 wt. %) element for CO at 200^{0}C. When CO concentration is 500 ppm, the sensitivity to CO already reaches to 10, while for 50 ppm CO it is 1.1 at 200^{0}C.

3.3 Sensing mechanism

The presence of a lone pair of electron on carbon atom of CO makes it a strong reducing agent and a reactive species. At slightly elevated temperature, with the help of lone pair of electron, CO undergoes an electronic action with metal ion of metal oxide. This leads in to the chemical adsorption of CO on oxide surface and also changes the resistance of sensor element. It is well known that, the resistance of metal oxides is strongly influenced by the presence of oxidizing or reducing gases. When the CO gas was introduced in the gas chamber, it may interact with oxide and then get deposited on its surface by emission of some quantity of heat, as adsorption is an exothermic process. At the varying temperatures, surface reaction and electronic flow is initiated by accumulation of gas on sensor surface. CO reacts with oxygen species adsorbed on the semiconductor (O_2^-, O^- and $O^{-\ -}$) increasing the conductance by releasing electrons on the metal oxide surface. Moreover, for the solid solution $La_{0.8}Sr_{0.2}CoO_3$, which is a well-known p-type semiconductor, the substitution of La^{3+} by Sr^{2+} increases the amount of oxygen vacancies and its sensitivity [13]. Following the literature, CO sensing by the investigated compound may adopt any one or both of the below given mechanisms.

3.3.1 Mechanism I

Oxygen in the atmosphere is adsorbed on the surface of sensor in the dissociated form to produce different species like O_2^-, O^- and O^{2-} (equation 1and 2). At the operating temperature, the adsorbed molecules of CO gas get oxidized in to CO_2 (equation 3 and 4) by interacting with adsorbed ionic oxygen species ($O^-_{(ads.)}$). When the sensor response measurement is carried out at higher temperature, the adsorbed gas undergo desorption and sensitivity was found to be reduced.

$$O_2 + M{-}O \rightarrow O_{2\,(ads.)} \quad (1)$$

$$O_{2\,(ads.)} + 2e^{-} \rightarrow 2O^-_{(ads.)} \quad (2)$$

$$O{-}M + CO \rightarrow O{-}M - - CO_{(ads)} \quad (3)$$

$$O{-}M - - CO_{(ads.)} + 2O_{(ads.)}{}^{-} \rightarrow O{-}M + CO_2 + e^- \quad (4)$$

3.3.2 Mechanism II

Being a reducing gas CO get adsorbed on the surface of the sensor element and may get reacted with bulk oxygen to form CO_2 gas with liberation of electron to the semiconductor surface (equ. 5 and 6). Now the oxygen deficient metal ion interacts with the adsorbed oxygen ion forming the metal oxide back (equa. 7 and 8). The adsorption of gas on the surface of metal oxide is an exothermic process. Heat evolved in this process acts as energy of activation and is utilized in combination of oxygen with CO to form CO_2. So formed CO_2 get desorbed as shown equation 6 and reduced active sites will generated by taking oxygen form air to continue adsorption and desorption process as shown in equations 7 and 8.

$$O{-}M + CO \rightarrow O{-}M - - CO_{(ads)} \quad (5)$$

$$O{-}M - - CO_{(ads)} \rightarrow M^+ + CO_2 + e^- \quad (6)$$

$$O^-_{(ads.)} + M^+ \rightarrow M^+ - - O^-_{(ads.)} \quad (7)$$

$$M^+ - - O^-_{(ads.)} \rightarrow M{-}O \quad (8)$$

$La_{0.8}Sr_{0.2}MnO_3$:Pd (1 wt. %) gave better sensitivity at 200^{0}C perhaps both mechanisms have favoured in this compound. It will be difficult to remove lattice oxygen from the surfaceof $La_{0.8}Sr_{0.2}MnO_3$ because of its high binding energy but incorporation of Pd increases the sensitivity and also facilitated the oxygen mobility on the surface and also created more adsorption sites on the surface.

4. Conclusion

Perovskite based $La_{1-x}Sr_xMnO_3$ have been developed for x = 0-0.2 as a chemical sensor for toxic gas as CO. When tested against CO, NH_3, H_2 and LPG, as a function of operation temperature, $La_{0.8}Sr_{0.2}MnO_3$ gave better sensor response at 270^0C. Noble metal Pd was impregnated with 0.5, 1 and 1.5% metal by weight in $La_{0.8}Sr_{0.2}MnO_3$ to see the on its gas sensing properties. At 200^0C, $La_{0.8}Sr_{0.2}MnO_3$:Pd (1 wt. %) gave higher sensor response than the other compounds. This element has been tested for the CO gas concentration range 50-400 ppm at 200^0C. Incorporation of Pd gave large CO response. Based on the present investigation and reported work, two probable mechanisms are suggested. $La_{0.8}Sr_{0.2}MnO_3$:Pd (1 wt. %) can be expected as a promising material to be used as CO gas sensor at an operating temperature as low as 200^0C.

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