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AMMONIA GAS SENSING PROPERTIES OF NANO-CRYSTALLINE BA DOPED LAMNO3 THICK FILM

A. V. Kadu[*1], N. N. Gedam[2] & S.G.Ibrahim[3]
[*1]Department of Chemistry, Prof Ram Meghe College of Engineering and Management, Badnera, Amravati, M.S. India.
[2]Department of Chemistry, Mahatma Jyotiba Fule Arts, Commerce & Science College, Bhatkuli- Amravati, M.S. India
[3]Department of Physics, Prof Ram Meghe College of Engineering and Management, Badnera, Amravati, M.S. India

ABSTRACT
In this work, we report the preparation and gas sensing performance of pure and doped $LaMnO_3$ were prepared by chemical method. The structural characteristics of the material were studied by using X-ray diffraction and transmission electron microscopy. The XRD pattern shows a nanocrystalline solid solution of $LaMnO_3$ with an orthorhombic phase and the crystallite sizes is found to be in the range of 30-40 nm. The gas sensing performance of the unmodified and surface modified films was tested for various gases such as H_2S, NH_3, LPG and CO. $La_{0.4}Ba_{0.6}MnO_3$ powder showed large response to 300 ppm NH_3 gas at an operating temperature 190^0C. The sensitivity, selectivity of $La_{0.4}Ba_{0.6}MnO_3$ thick films was measured

KEYWORDS: NH_3sensor, $La_{0.4}Ba_{0.6}MnO_3$, Gas sensing properties, Response time.

I. INTRODUCTION
Gas sensors are very important in many fields, such as industrial emission, household security, vehicle emission control, environmental monitoring, food nutrition and safety etc. [1-3]. Among them, ammonia sensors have attracted great attention due to their applications in many fields of technological importance, such as food technology, chemical engineering, medical diagnosis, environmental protection, monitoring of car interiors and industrial processes [4].

Semiconducting metal oxides have shown considerable impact in gas detection due to their low cost and flexibility in production, simplicity in use, large number of detectable gases and various application fields [5]. However, few of them are suitable to all requirements of gas sensors with high sensitivity, short response and recovery time, low detection limit, good selectivity and long-term stability. Recently, some composite oxides such as spinel [6] and perovskite [7] were found to be more attractive than single-metal oxides for their better selectivity and/or sensitivity to certain gases.Lanthanum perovskites ($LaMO_3$) containing metals of the first transition series are very appealing functional materials because of their immense technological potential. Some are used as membranes for separation processes or as gas sensors in automobiles, several show magneto-optic or magneto resistant properties.

In the present study, different compositions of $La_{1-x}Ba_xMnO_3$ powders were prepared using sol–gel citrate process and are characterized using XRD and TEM techniques. The gas sensor based on the nanocrystalline $La_{0.4}Ba_{0.6}MnO_3$ material shows good sensitivity and selectivity to the ammonia gas.

II. EXPERIMENTAL DETAILS

Material Synthesis
All reagents of analytical grade were used. Nanostructured $LaMnO_3$ and $La_{1-x}Ba_xMnO_3$ were synthesized separately using chemical routes. The precursor was prepared by sol–gel citrate method by using stoichiometric

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ratio of lanthanum nitrate, manganese nitrate, barium nitrate and citric acid. Further it was dissolved in ion-free water at 80^0C for 2 h. Then ethylene glycol was added under constant stirring to obtain a homogeneous and stable sol. The solution was further heated in pressure vessel at about 130^0C for 12 h. During this reaction transparent solution was transform into a gel state with very high viscosity. The material was then heated in a furnace at 350^0C for 3 h and a violent combustion was occurs which spontaneously propagates until all the gel was burnt out to form a loose powder. The powder was then calcined at 650^0C for 6 h in order to improve the crystallinity of materials.

Characterization techniques

The synthesized samples were characterized for their structure and morphology by X -ray powder diffraction (XRD; Siemens D5000) and transmission electron microscopy (TEM; Hitachi-800). The X-ray diffraction data were recorded by using CuK_α radiation (1.5406 A^0). The intensity data were collected over a 2θ range of 10–70^0.

Measurement of sensing properties

The gas-sensing properties of prepared $La_{1-x}Ba_xMnO_3$ powders were studied for reducing gases such as hydrogen sulphide (H_2S), ammonia (NH_3), liquefied petroleum gas (LPG) and carbon monoxide (CO) whose concentration were fixed at 1000 ppm in air. The gas sensitivity (S) was defined as: $S = (Ra - Rg)/Ra = \Delta R/Ra$; where, Ra and Rg are the resistance of sensor in air and the test gas, respectively. The gas-sensing properties were measured in a temperature range of 50 – 350^0C.

III. RESULTS AND DISCUSSION

X-ray Diffraction Study

The XRD pattern of the $La_{0.4}Ba_{0.6}MnO_3$ prepared by sol-gel citrate method calcined at 650^0C is presented in Figure 1. The XRD peaks correspond to an orthorhombic phase and no other peaks observed are indicating the absence of any other phase or impurities. The XRD pattern indicates that the product has high degree of crystallinity judged from the high and sharp diffraction peaks. The average particle size of the nanocrystalline $La_{0.4}Ba_{0.6}MnO_3$ according to the scherrer formula were in the range of 30–40 nm.

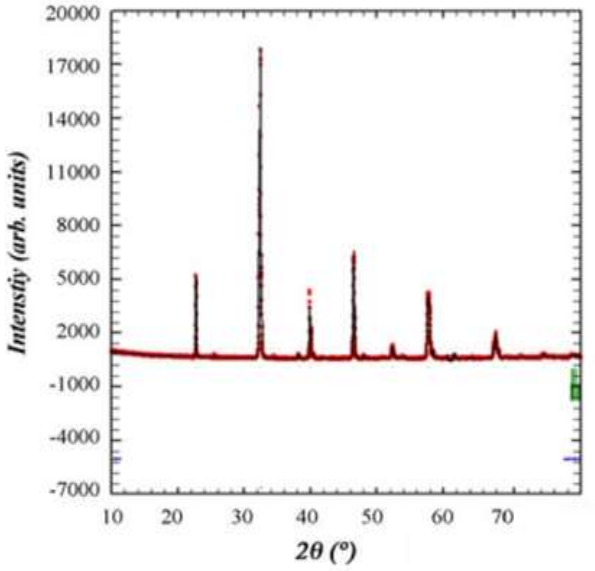

Fig 1 XRD pattern of $La_{0.4}Ba_{0.6}MnO_3$ calcined at 650^0C

Scanning electron microscopy

The morphology of the powder sample has been observed by SEM. Figure 2 shows the SEM micrograph of the $La_{0.4}Ba_{0.6}MnO_3$ powder with uniform grain size distribution having a small tendency of agglomerates formation**.** The particle shapes are not well defined. Many large and small pores are present in the whole material. We assumed that the pores are mainly intergranular because intragranular pores are not seen on the SEM photograph.

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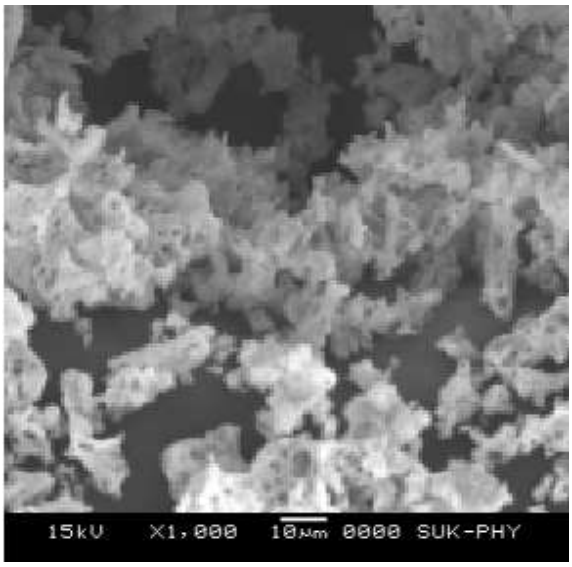

Fig 2 SEM image of $La_{0.4}Ba_{0.6}MnO_3$, calcined at 650^0C

Gas Sensing Properties

Figure 3 shows the sensor response (*S*) as a function of operating temperature for undoped $LaMnO_3$ nanopowder calcined at 650ºC for 6 h for various reducing gases like NH_3, LPG, CO and H_2S. The sensor characteristic shows higher response for NH_3 gas as compared to LPG, CO and H_2S at an operating temperature 250ºC.

In order to improve the gas response properties, a great variety of atoms or additives are introduced in the base sensing semiconductor. Figure 4 shows the gas response as a function of different amount of Ba doped $LaMnO_3$ (x = 0.2, 0.4, 0.6 and 0.8). The response to NH_3 gas goes on increasing with increasing amount of Ba. The largest response for $La_{0.4}Ba_{0.6}MnO_3$ (x = 0.6) was obtained due to more available sites for the oxygen to be adsorbed and in turn to oxidize the test gas. The decrease in response may be due to the insufficient number of sites available on the surface. The partial replacement of La by Ba ion results in decrease in grain size, which results in larger density of grain boundaries, which increases film's effective exposure area to the ammonia gas. The chemical composition of the semiconductor is also a key parameter that influences their sensing performance. In fact, composition by itself can affect the microstructure and, thus determine the sensing properties.

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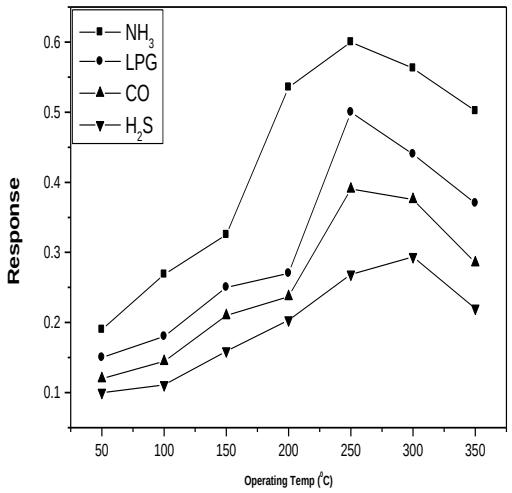

Fig 3 Gas sensing characteristics of undoped $LaMnO_3$ for various reducing gases as a function of operating temperature.

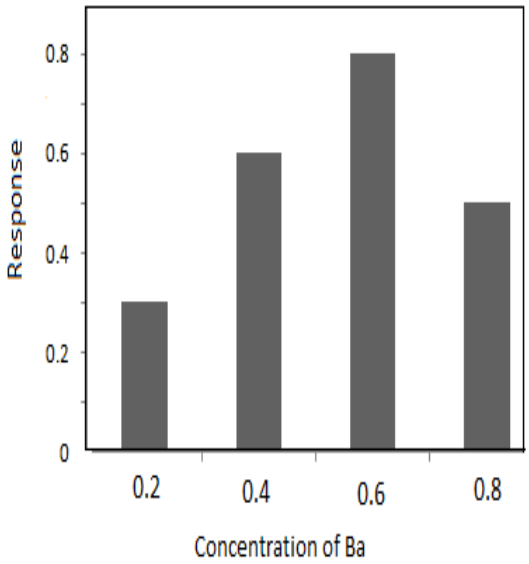

Fig 4 Sensor Response of $LaMnO_3$ doped with different amount of Ba calcined at 650^0C. (a) x = 0.2, (b) x = 0.4, (c) x = 0.6 and (d) 0.8

Figure 5 illustrates the gas response of $La_{0.4}Ba_{0.6}MnO_3$ at different operating temperature. It is observed that the sensor has high response to NH_3 gas as compared to LPG, CO and H_2S at 190^0C. The high response to NH_3 gas can be attributed to the surface modification by Sr over $La_{0.4}Ba_{0.6}MnO_3$ film. The improved selectivity is possibly explained as follows: When O^{2-}, is adsorbed on the $La_{0.4}Ba_{0.6}MnO_3$ surface, it traps electron(s) from the body of the n-type semiconductive $La_{0.4}Ba_{0.6}MnO_3$ due to the strong electronegativity of the oxygen atom to produce negatively charged chemisorbed oxygen such as O_2^-, O^- and O^{2-}. As the result, the concentration of electrons in the n-type $La_{0.4}Ba_{0.6}MnO_3$ decreases and hence the resistance of the material increases.

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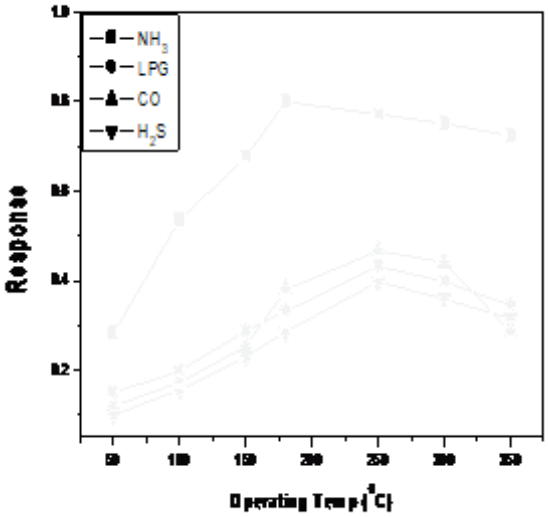

Fig 5 Response to different reducing gases of $La_{0.4}Ba_{0.6}MnO_3$ as a function of operating temperature.

Figure 6 shows the dependence of gas response of the $La_{0.4}Ba_{0.6}MnO_3$ sensor on the concentration level of NH_3 at 190ºC. It is clear from the graph that with the increase in the concentration, the response increases linearly up to 200 ppm of NH_3, after that it saturates. The graph also indicates that at low concentration response has a linear relationship with concentration because there may be sufficient number of available surface states to act on NH_3 vapour. After 200 ppm level of NH_3, the curve flattens because there would not be enough ionosorbed oxygen species to contribute to detecting mechanisms.

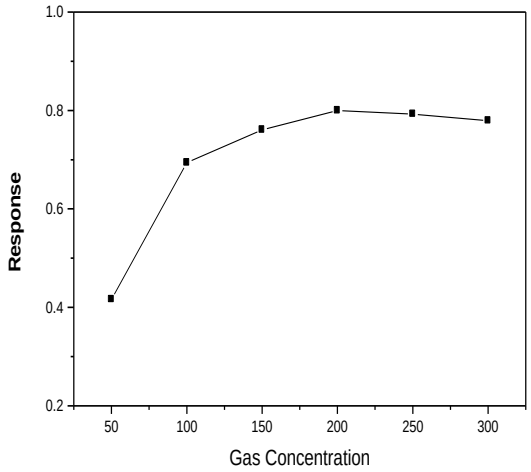

Fig 6 Response of $La_{0.4}Ba_{0.6}MnO_3$ to NH_3 gas of different concentration at an operating temperature 180ºC.

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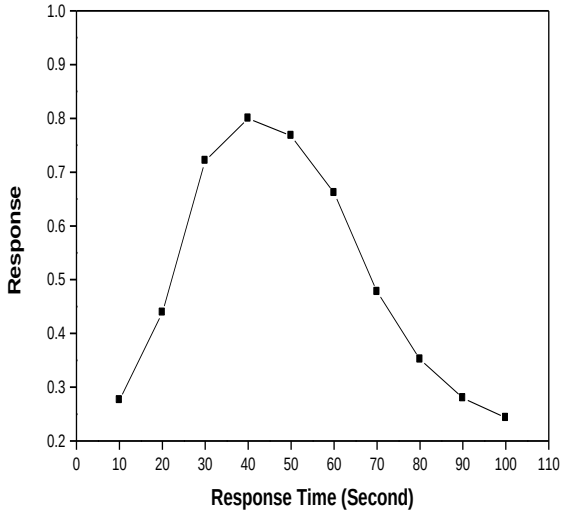

Fig 7 Response characteristics of $La_{0.4}Ba_{0.6}MnO_3$ at 180°C.

Figure 7 shows the response time of the sensor at 180oC. The response time in this case is ~ 40 sec. It was observed that the response time comes to saturated at 55 sec. It suggests that after this time there is no more O– species left to react with the ammonia vapour. It also indicates that by increasing the surface area i.e. increasing the grain size of the film, one can increase the response time.

IV. CONCLUSION

$La_{0.4}Ba_{0.6}MnO_3$ thick film was prepared by sol-gel citrate method. XRD of $La_{0.4}Ba_{0.6}MnO_3$ calcined 650^0C for 6 h showed good crystalline quality with a grain size 40 nm. It was also found that $La_{0.4}Ba_{0.6}MnO_3$ sensor exhibited excellent gas response and selectivity for NH_3 gas at 190^0C. The sensor is very promising for NH_3 gas detection with a response time in second range.

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