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LPG- sensing properties of perovskite $BiFe_{0.6}Mn_{0.4}O_3$ nanomaterials

G. N. CHAUDHARI
Nano Technology Research Laboratory, Department of Chemistry, Shri Shivaji Science College, Amravati- 444602, M.S., India

Nanocrystalline $BiFeO_3$ doped with manganese were synthesized by sol-gel citrate method and studied for gas sensing behavior to reducing gases like liquefied petroleum gas (LPG), CO, CH_4 and NH_3. X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) were used to characterized the composition, phase and particle size of these ferrites. The XRD pattern of the $BiFeO_3$ shows rhombohedral distorted perovskite structure with an average crystallite size of 35-40 nm. The maximum sensitivity was obtained $BiFe_{0.6}Mn_{0.4}O_3$ sensor at an operating temperature 250 ^{o}C for LPG. Incorporation of 0.8 wt% Pd improved the sensitivity, selectivity, response time and reduced the operating temperature from 250 to 210 ^{o}C for LPG sensor. The response time for 1000 ppm LPG is less than 1 minute at 210 ^{o}C.

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Keywords: $BiFe_{0.6}Mn_{0.4}O_3$, LPG sensor, Selectivity, Response time

1. Introduction

The development of gas sensors to monitor combustible gases is imperative due to the concern for safety requirements in homes and for industries, particularly for detection of LPG, which is one of extensively used but potentially hazardous gases, because explosion accident may be caused when it leaks out accidentally or by mistake. So the detection of LPG is necessary for domestic appliances.

Gas sensing applications of nanocrystalline materials have received considerable interest in recent years [1]. There have been attempts to use different materials as hydrocarbon sensors, but good sensitivity has been obtained only on some like ZnO or SnO_2 modified with Pt [2-4] etc. Supported platinum is, however, not as selective as one would desire and also it acts as a sensor for H_2 and ethanol as well. Pd dispersed on Fe_2O_3 detects hydrocarbons, but with low sensitivity [5]. Chaudhari et.al. [6] have succeeded in preparing nanocrystalline $BaTiO_3$ thick film for LPG sensor by employing sol-gel method. Current years have seen increased interest in searching new semiconducting materials for LPG sensing application.

Thus, it is of great interest to find new metal oxide materials to develop LPG gas sensors with enhanced performances. It is well known that a number of pervoskite oxides (ABO_3) were used as gas sensor materials because of their stability in thermal and chemical atmospheres [7-9]. A semiconductor gas sensor presents the property of changing the conductivity of the sensing material when this is exposed to different gas atmospheres. The gas sensing mechanism usually depends on the operating temperature. The optimum working temperature of the semiconductor sensor depends on the gas atmosphere and on the properties of the sensor material selected in every case [10,11].

In recent years, the ferrites have demonstrated to be good materials for semiconductor gas sensors [12-14]. Bismuth ferrites $BiFeO_3$, $Bi_4Fe_2O_3$ and $Bi_2Fe_2O_9$, as well as $Bi_4V_2O_{11}$ are disclosed as being useful as sensitive compounds for detecting acetone, ethanol or gasoline vapors and natural gas [15].

The present work was undertaken to investigate the structural and gas sensing behavior of $BiFeO_3$ nanoparticle prepared by a sol–gel citrate method. In an attempt to improve the sensitivity and selectivity of $BiFeO_3$ have been replaced with Mn in place of Fe atom. The results showed that $BiFe_{0.6}Mn_{0.4}O_3$ was very promising in detecting LPG at an operating temperature 250 ^{o}C due to its high response and selectivity. Further Pd incorporation, the operating temperature for maximum sensitivity decreased 250 to 210 ^{o}C and response time decreases to few second.

2. Experimental details

2.1 Preparation and characterization of samples

The samples with the composition $BiFe_{1-x}Mn_xO_3$ (x= 0, 0.2, 0.4 and 0.6) were prepared by sol–gel citrate method. The followings analytically pure grade $Bi(NO_3)_2{\cdot}6H_2O$, Fe $(NO_3)_2{\cdot}9H_2O$, and Mn $(NO_3)_2{\cdot}3H_2O$, were used as starting materials. A solution containing appropriate amount of metal nitrates was mixed with citric acid and ethylene glycol. The resultant mixture was stirred magnetically at 80 ^{o}C for 2 h to get homogeneous mixture. The solution was further heated in pressure vessel at about 130 ^{o}C for 12 h. The dried material was ignited in air, at 350^{o}C and a violent combustion wave occurs which spontaneously propagates until all the gel was burnt out to form a loose powder. The dried powder then calcined at 550 °C in order to improve the crystallinity of ceramic. Noble metals palladium was incorporated in the samples. An appropriate quantity of corresponding $PdCl_2$ solution was added to the nitrating mixture.

The synthesized samples were characterized for their structure by powder X-ray diffraction (XRD) using a Siemens D 5000 diffractometer .The XRD data were recorded by using Cu K_α radiation (1.5406 A°). The intensity data were collected over a 2θ range of 20–60°. The average crystallite size of the samples was estimated with the help of Scherrer equation using the diffraction intensity of all prominent lines [16]. Transmission Electron Microscope (TEM) examination of the synthesized powder was performed using an H-800 electron microscope.

2.2. Measurement of sensors

The nanometer size powders obtained above were mixed with a suitable amount of an adhesive, and were ground into paste. Then, the paste was packed into an alumina tube on which two electrodes had been installed at each end. The ceramic tube was about 10 mm in length, 2 mm in outer diameter, and 1.5 mm in inner diameter. To improve stability and repeatability, the gas sensors were calcined at 600 °C for 1 h. The gas-sensing properties were measured in a temperature range of 50–350 °C.

The gas sensitivity (*S*) is defined as the ratio of the change of resistance in presence of gas (R_g) to that in air (R_a) [17],

$$S = (R_a - R_g)/R_a = \Delta R/R_a$$

In the region of saturation, 'S' reaches values near to unity. In order to calculate the sensitivity, the electrical resistance of the element was measured in the presence and absence of LPG taken in a concentration of 1000 ppm in dry air. The cross sensitivity of the sensor element to other reducing gases like LPG, NH_3, CO and CH_4 gas was also studied.

3. Results and discusition

3.1. Structural characterization

Fig. 1 shows the XRD pattern of the $BiFeO_3$ synthesized at 550°C with rhombohedral distorted perovskite structure according with JCPDS 200169. A definite line broadening of diffraction peaks gives an indication that the synthesized materials are in nanometer range. The crystallite size was calculated from Scherrer formula applied to the major peaks and was found to be around 35-40 nm. The XRD spectra of $BiFe_{0.6}Mn_{0.4}O_3$ has a majority $BiFeO_3$ phase crystallization.

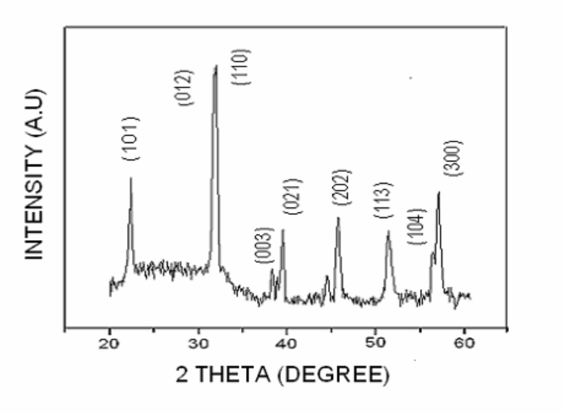

Fig. 1. XRD pattern of $BiFeO_3$ calcined at 550 °C.

Fig. 2 shows the TEM micrograph of $BiFe_{0.6}Mn_{0.4}O_3$ nanoparticle calcined at 550°C. TEM pattern shows the samples were all spherical particles with uniform grain size distribution. As we can see, the results observed from TEM image were in agreement with those calculated by Scherrer formula according to XRD experiments.

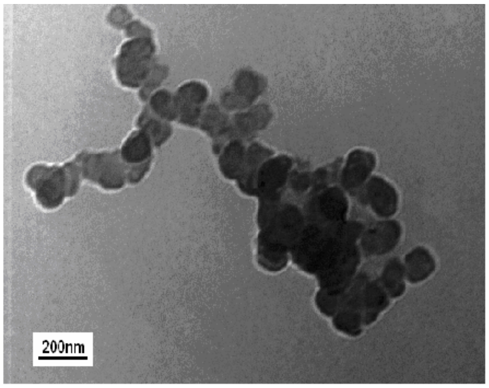

Fig. 2. TEM micrograph of the $BiFe_{0.6}Mn_{0.4}O_3$ calcined at 550 °C.

3.2 Gas sensing characteristics

LPG is a mixture of hydrocarbons like n-propane and n-butane and one of the byproducts after partial combustion is CO and after complete combustion it is CO_2 and H_2O. Hence, the sensitivity of the sensor to other reducing gases like CO and CH_4 were also measured as a function of operating temperatures. Fig. 3 shows the gas sensing measurements of $BiFeO_3$, for various reducing gases such as Liquid petroleum gas (LPG), CO, NH_3 and CH_4 at various operating temperature. It is clear from the graph that the sensitivity to LPG is more than other reducing gases. For LPG the sensitivity increased and reached saturation value around 250 °C, whereas the sensitivity to other gases was low and decreased with increased in temperature. Nanostructuring of the base semiconducting oxide also contributes to the improvement in the gas response by larger surface area because here the complete particle contributes to the gas sensing phenomenon. The larger surface area of the materials synthesized also facilitates the gas detection at much lower temperatures [18].

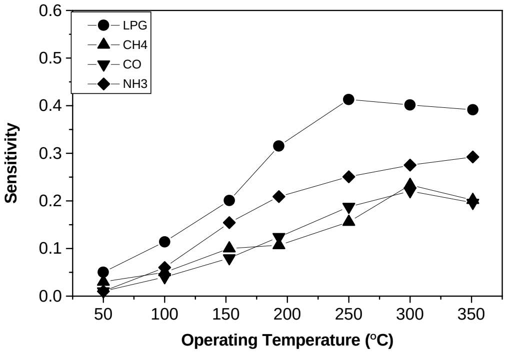

Fig. 3. Gas sensing characteristics of $BiFeO_3$ at different operating temperatures for various reducing gases

In order to enhance the gas sensitivity, dopants were shows to effective influence for semiconductive properties of sensor materials. Three samples with the composition $BiFe_{1-x}Mn_xO_3$ (with x=0.2, 0.4 and 0.6) were studied as a LPG sensor and found that it depends on the operating temperature and Mn content. Fig. 4 shows the gas sensitivity for all the samples in the presence of the LPG, at various operating temperatures. The sensitivity increases with increasing temperature and reaches a maximum value corresponding to an optimum operating temperature. For the $BiFe_{0.6}Mn_{0.4}O_3$ shows increase in sensitivity to maximum value of 7.2 at an operating temperature 250 °C, whereas the other samples ($BiFe_{0.8}Mn_{0.2}O_3$ and $BiFe_{0.2}Mn_{0.8}O_3$) show lower sensitivity to LPG. Compared with $BiFeO_3$, $BiFe_{0.6}Mn_{0.4}O_3$ showed the large response to LPG. The reason may be that the partial replacement of Fe ions by Mn ions at the B-sites is advantageous to adsorption and oxidization for LPG. In addition, the partial replacement results in a decrease of grain size and hence in an increase of surface area. Since small grains have relatively large grain boundary areas, the adsorption of LPG molecules is relatively high.

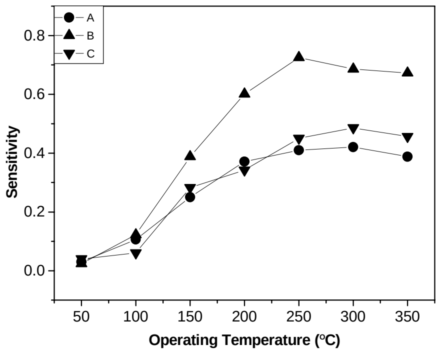

Fig. 4. Sensitivity of $BiFe_{1-x}Mn_xO_3$ for LPG sensor calcined at 550 °C. (A) x=0.2, (B) x= 0.4, (C) x=0.6.

The sensitivity of the sample $BiFe_{0.6}Mn_{0.4}O_3$ to reducing gases such as LPG, CO, NH_3 and CH_4 was also investigated at an operating temperature 250 °C. As can be seen from Fig. 5, the sensitivity of this sensor is remarkably higher for LPG than for other gases. For these experiments, the resistance was measured during cooling the sample after being heated to sufficiently high temperature, thereby securing a good reproducibility of the sensitivity–temperature characteristics. It is clear that this material is the most sensitive to LPG and less sensitive to the others.

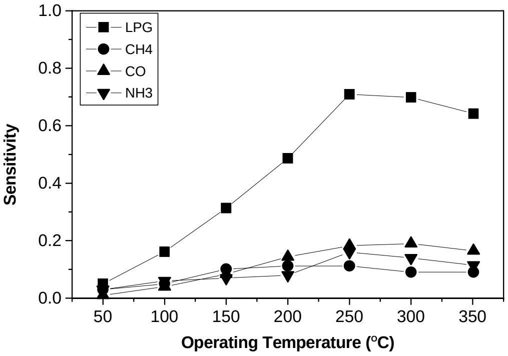

Fig. 5. Cross sensitivity as a function of operating temperature for $BiFe_{0.6}Mn_{0.4}O_3$ calcined at 550 °C for various reducing gases.

3.3. Effect of palladium incorporation on the gas sensing characteristics

Palladium is proved to be highly effective in improving the sensitivity of semiconducting oxides for reducing gases [19]. In addition, palladium is known to have a catalytic effect due to its excellent oxidation capability to convert hydrocarbons at lower temperatures and making the sensor selective to hydrocarbons [20]. The effect of Pd loading on the sensitivity of sensor at various operating temperature as shown in Fig. 6 the Pd concentration was varied from 0.1 to 1.4 wt.%. It was observed that 0.8 wt.% Pd was the optimum concentration for maximum sensitivity to LPG at 210°C. The increase in sensitivity when the Pd concentration is increased from 0.1 to 0.8 wt.% and then decreased above 0.8 wt.% Pd that suggests the importance of the dispersion of Pd on the semiconductor surface [21]. Pd incorporation decreased the operating temperature from 250 to 210 °C. The reduction in temperature is considered to very beneficial from the sensor point of view. Fig. 7 shows 0.8 wt.% Pd doped $BiFe_{0.6}Mn_{0.4}O_3$ shows better sensing characteristics for LPG at an operating temperature 210 °C and lower to other reducing gases.

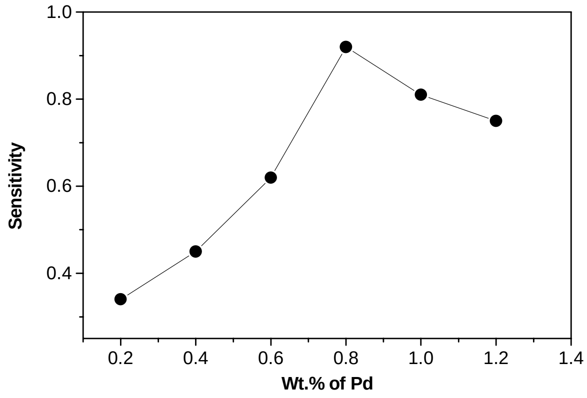

Fig. 6. Sensitivity with different concentration of Pd doped $BiFe_{0.6}Mn_{0.4}O_3$ calcined at 550 °C for LPG sensor.

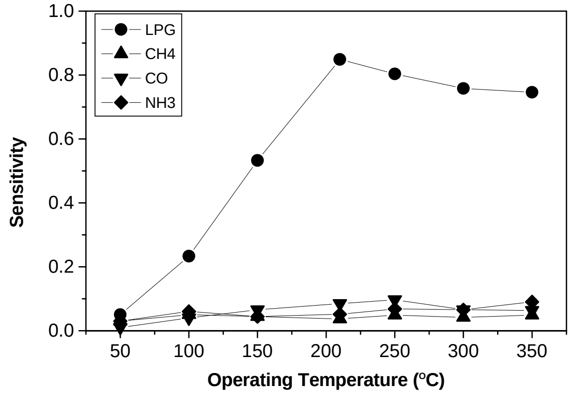

Fig. 7. Gas sensitivity as a function of operating temperature for 0.8 wt. % Pd doped $BiFe_{0.6}Mn_{0.4}O_3$ calcined at 550 °C for various reducing gases.

The variation in sensitivity of 0.8 wt% Pd doped $BiFe_{0.6}Mn_{0.4}O_3$ toward LPG concentration (in ppm) at 210° C is shown in Fig. 8. In general, the sensitivity of the gas sensor increases with the increase of the concentration of sensing gas in air. For the gas sensor investigated, the magnitude of sensor response increased linearly with LPG concentration up to 1000 ppm and it is observed that the sensor have tendency to saturated at gas concentration above 1000 ppm. Fig. 9 clearly shows that the response characteristics for 0.8 wt% Pd doped $BiFe_{0.6}Mn_{0.4}O_3$ are faster than the $BiFe_{0.6}Mn_{0.4}O_3$ to 1000 ppm LPG. The effect of Pd thus seen not only increases in sensitivity to LPG considerably but also the increase in rate of response. This kind of sensitization has been well explained by an electronic nitration between the noble metal and the semiconducting oxide [22].

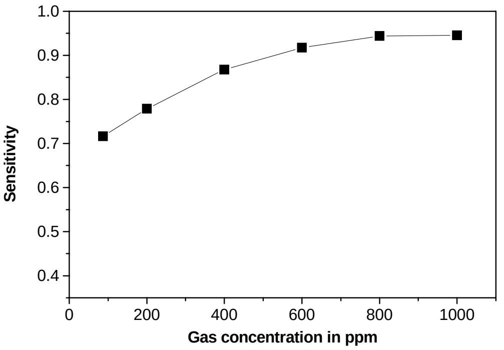

Fig. 8. Sensitivity of 0.8 wt.% Pd doped $BiFe_{0.6}Mn_{0.4}O_3$ calcined at 550 °C for LPG concentration (in ppm).

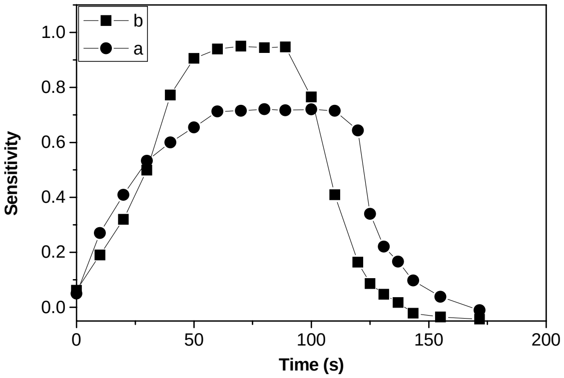

Fig. 9. Response characteristics of ((a) $BiFe_{0.6}Mn_{0.4}O_3$ calcined at 550 °C and (b) 0.8 wt. % Pd doped $BiFe_{0.6}Mn_{0.4}O_3$ calcined at 550 °C.

4. Conclusion

- Nanocrystalline $BiFeO_3$ and $BiFe_{0.6}Mn_{0.4}O_3$ were synthesized by using sol-gel citrate method and the XRD pattern of the $BiFeO_3$ shows rhombohedral distorted perovskite structure.TEM image shows that $BiFeO_3$ was spherical particles with uniform grain size distribution and an average crystallite size of 35-40 nm.
- A sensitivity study for reducing gases is carried out to demonstrate that $BiFe_{0.6}Mn_{0.4}O_3$ is highly selective and sensitive to LPG at an operating temperature 250°C.
- The 0.8 wt% Pd incorporation lowers the operating temperature from 250 to 210°C and enhances the LPG sensitivity. The sensor based on these

material showed excellent sensor response and selectivity to LPG at 1000 ppm.

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*Corresponding author: cgnroa@yahoo.com