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Synthesis, Characterization and Gas Sensing Performance of $PbMnO_3$, $PbMnO_3$: SiO_2 and $PbMnO_3$: Al_2O_3

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ABSTRACT

The present study reports ecofriendly mechanochemical synthesis of $PbMnO_3$, $PbMnO_3$:SiO_2 and $PbMnO_3$:Al_2O_3 composite metal oxides for the first time. The polycrystalline product obtained was analyzed by various physical investigative techniques including FTIR, XRD, SEM, TEM and BET surface area. Screen printed thick films of $PbMnO_3$ and modified $PbMnO_3$ oxides were prepared to check the potential application for gas sensing properties for most toxic, combustible and hazardous gases CO, CO_2, H_2, Cl_2, NH_3 and H_2S at different operating temperatures ranging from 50^{0}C to 400 ^{0}C. Among the synthesized sensor $PbMnO_3$:SiO_2 shows highest sensitivity (1740) towards NH_3 at 50 ^{0}C as compared to$PbMnO_3$ (71.42) to NH_3 at 200 ^{0}C and$PbMnO_3$:Al_2O_3 (315.8) toH_2S at 250^{0}C.This study signifies that sensor was observed to be highly sensitive and selective to NH_3 and H_2S gas.

Keywords : $PbMnO_3$, XRD; BET, Thick Films, Gas Sensing

I. INTRODUCTION

In recent years, there has been interest in perovskite type of metal oxides containing manganese. These materials show interesting magnetic and electric properties, such as magneto resistivity, nanoscale charge ordering and high oxygen ion conductivity, opening the way to potential applications [1–3]. Gas detection problem was overcome by modified metal oxide semiconducting material. Due to the different applications and inherent limitations of different gas sensing technologies, researchers have been working on different scenarios with enhanced gas sensor calibration. Since 1962 it has been known that absorption or desorption of a gas on the surface of a metal oxide changes the conductivity of the material, so it brings high value of nanocrystalline thick film technology. This phenomenon being first time reported by Sieyama et.al. [1] for zinc oxide thick film.

The response of semiconductor-based sensors is due to the equilibration of oxygen in the gas phase with ionic and electronic point defects in the oxide semiconductor. The metal oxide most generally used in such sensors is SnO_2, but some other oxides like TiO_2 and WO_3, are also used. The perovskite structure obtained from a wide variety of oxides with predominantly ionic conduction transport properties to predominantly electronic conduction. Due to high melting property perovskite, they possesses microstructural and morphological stability which is important characteristics to be a long term sensor. Apart from this property, the perovskite structure has two differently-sized cations, which makes possible addition of dopant to it. This doping flexibility is useful for control of the transport and catalytic properties so as to optimize sensor performance for particular applications.

In the market non-dispersive infrared absorption (ND-IR) CO_2 gas sensors available which are bulky and have high cost [12, 13]. Metal oxides and

modified metal oxides have always been the choice for CO_2 sensor materials [14-18]. Ammonia (NH_3) and H_2S is a toxic gas with threshold limit value of 25 ppm for long term exposure (8 h) which are detected by semiconductor metal oxides including SnO_2, WO_3 and RuO_2 doped ZnO have been reported for detection of NH_3 [19,20]. The operation of these sensors is based on the reversible change of electrical conductance (resistance) which show rise in power consumption reduces sensor life and complicates the design of the sensor [21]. Hence there is need to develop and introduce gas sensor for detecting ammonia (NH_3) and H_2S gas for environmental monitoring in chemical industries and research laboratories. Investigation for new and excellent sensor material with their new properties of ordinary material has becomes an important area for research. The doping and coating of metal ion increases the surface area of metal oxide semiconductors which increases the surface area of gas sensor. Hence keeping this view in mind in the present study first time we report on the synthesis of nanocrystalline Lead mangnate oxide ($PbMnO_3$) by mechanochemical method, SiO_2 composite and Al_2O_3 composite with $PbMnO_3$ by hydrothermal method and report as semiconductor-based gas sensors. Various gases like NH_3, CO_2, Cl_2, H_2S, CO and H_2 at different operating temperature by keeping fixed gas concentration and finally selectivity of different tested gases is compared with each other using these metal oxides. This sensor was observed to be highly sensitive and selective to NH_3 and H_2S gas. Further the synthesized nanostructure powders were characterized by XRD, SEM, TEM and BET surface area.

II. EXPERIMENTAL

2.1 Materials and Reagents:

Reagents used in this study were purchased and used without further purification: Lead oxide (PbO), Sigma-Aldrich, 99.99 %), Manganese oxide (MnO_2, Sigma-Aldrich, 99.90 %), sodium hydroxide (NaOH, Merck, 99 %). All gases required were prepared in laboratory by various chemical reactions.

2.2 Synthesis of $PbMnO_3$:

Synthesis of perovskite was performed by various techniques which include co-precipitation [17], sol-gel method [18] and thin film vapour deposition method [19]. These methods are laborious, expensive and cause water pollution. In this study, we have synthesized $PbMnO_3$ by green chemistry approach with mechanochemical process. The mechanochemical procedures are environmentally friendly. The method allows accelerating and facilitating the synthesis processes producing negligible gas emission. It is fast and ecologically pure. In this method, equimolar mixture of Analytical Grade PbO and MnO_2 was grinded with mortar and pestle to attain fine powder for 20 min and heated at 500 ^{0}C for 3 h. Again the obtained powder was further heated at 800 ^{0}C following milling after each interval of three-hour time. The rise in temperature of muffle furnace was programmed at the rate 10 ^{0}C/min from one temperature to the temperature for 12 h. After heating at 500 ^{0}C the material was cooled and grounded with gap of 1 h using mortar and pestle. Later on, the ground material was further heated at 800 ^{0}C for another 12 h. Finally, polycrystalline powder of $PbMnO_3$ obtained was used for further characterization preparation of composite metal oxides and for gas sensing performance.

2.3 Synthesis of composite $PbMnO_3$:SiO_2:

The $PbMnO_3$:SiO_2 sensor was prepared by mixing definite amount of SiO_2 solution (1 mol %) with synthesized $PbMnO_3$ powder (1 mol %) along with buffer solution. The slurry obtained was stirred for 1 h and transferred into steel lined Teflon autoclave and kept in the oven at 120 °C for 24 h. The precipitate obtained was filtered washed with distilled water and dried at 100 °C for 12 h. The brown polycrystalline product was directly placed in the furnace for calcination at 300 °C for 4 h.

2.4 Preparation of composite $PbMnO_3$:Al_2O_3:

The $PbMnO_3$:Al_2O_3 sensorwas prepared by mixing equimolar amount of Al_2O_3 solution (1 mol %) with synthesized $PbMnO_3$ powder (1 mol %) along with buffer solution. The slurry obtained was stirred for 15 min. and after stirring this solution was transferred into steel lined Teflon autoclave and kept in the oven for 24 h at 100°C. Finally the obtained product $PbMnO_3$:Al_2O_3 was filtered washed with demonized water and dried at 100 °C for 24 h in the oven. The obtained polycrystalline product was heated at 400 °C for 3 h. The obtained products $PbMnO_3$, $PbMnO_3$:$SiO_2$and $PbMnO_3$: Al_2O_3 were checked for its potential application as a gas sensor.

2.5 Characterization:

The XRD profile was obtained recorded on a multipurpose X-ray diffractometer (Philips-1710 diffractometer with CuKα, λ = 1.5406 Å) at a scan rate of 0.17° 2θ S^{-1}.The scanning electron microscope (SEM) electron micrograph images were taken on a Hitachi SU 70 FESEM with a Schottky electron gun. The Structure and particle size of the synthesized materials were carried out using TEM with SAED on CM-200, Phillips microscope. Quantachrome Autosorb Automated Gas Sorption System Autosorb-1, NOVA-1200 and Mercury PorosimeterAutosorb-1c was used to obtain BET surface area.

2.6 Thick film preparation and gas sensing measurements:

The uniform thick paste of synthesized gas sensing materials $PbMnO_3$ and its composite was prepared by thoroughly mixing its fine powder with 30 wt % organic binder (ethyl cellulose), 30 wt % solvent (2-butoxyethanol and terpineol) and 15 ml dispersant. The films were prepared on glass substrate by using screen printing followed by drying under tungsten filament lamp. Dried films were fired at 450 °C for 1 h for the complete removal of organic binder. The gas sensing property of three sensors have been studied using static gas sensing system towards various gases.

The current developed was measured by a digital Picoammeter by applying constant voltage to the sensor. The current passing through the heating element was monitored using with an electronic circuit with adjustable on-off time intervals. A Cr-Al thermocouple was used to sense the operating temperature of the sensor. The output of the thermocouple was connected to a digital temperature indicator. The heater was fixed on the base plate to heat the sample up to required operating temperatures. A gas inlet valve was fitted to the base plate, the required gas concentration inside the static system was achieved by injecting a known volume of a gas using gas injecting syringe. The air was allowed to pass into the glass chamber after every gas exposure cycle. The complete illustration of gas sensing apparatus is shown in Fig. 1.

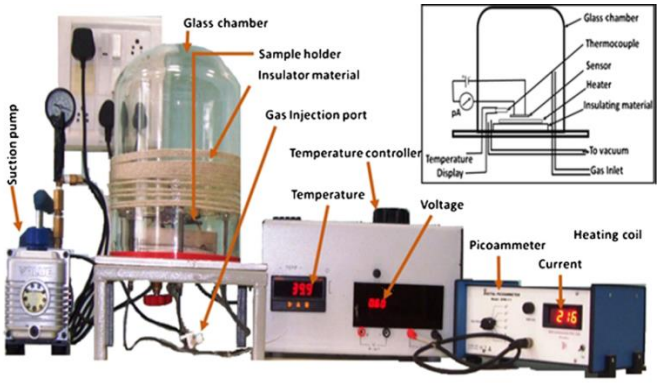


Fig 1. Steady gas sensing system photograph with block diagram

Finally the sensitivity of thick films were checked for NH_3, H_2S, H_2, CO_2, CO and Cl_2 gases for the temperature range of 50°C to 400 °C with various gas concentration (50-100 ppm). The changes in resistance on contact between target gas and sensor were measured from steady gas sensing system. The ratio of change in conductance of sample on exposure to a test gas (G_{gas}) to the conductance in air (G_{air}) is known as sensitivity and is simply defined as,

$$\text{Sensitivity} = \frac{G_{gas} - G_{air}}{G_{air}}$$

Where R_a is the resistance of metal oxide film in the presence of dry air and R_g the resistance of metal oxide film in presence of test gas.

III. Results and Discussion

3.1 General:

Hydrothermally synthesized products ($PbMnO_3$:$SiO_2$and $PbMnO_3$:Al_2O_3) were calcined at 600 °C for 3 h to remove organic matter and then analyzed by X-ray diffraction method. XRD pattern obtained for all three product shows that they are polycrystalline in nature. The XRD pattern recorded for pure $PbMnO_3$ (Fig. 2a) shows 2θ values along with (hkl) planes at 26.34 (110), 29.06 (100), 30.5 (100), 32 (110), 50.74 (200). These peaks in the XRD profile well matches with JCPDS data (Card No. 254301) and confirm the crystals are cubic in nature. Figure 2b gives XRD pattern for $PbMnO_3$:SiO_2. The 2θ values in connection with (hkl) plane are 26.4 (100), 26.52 (110), 28.72 (222), 38.4 (102), 44.4 (110), 52.3 (200) 59.3 (220). The recorded XRD pattern shows there is no any amorphous phase found and it reveals that product is highly polycrystalline with cubic in nature. The XRD analysis of $PbMnO_3$:Al_2O_3 shows sharp peaks at 33.96 (100), 34 (200), 38.5 (100), 47.46 (110), 52.4 (101) and extra peaks due to Al coating at 2θ values 25.7, 37.8, 40.8 and 51.9 (Fig. 2c). All these obtained peaks are well relevant to JCPDS card number data confirming with cubic structure.

The SEM analysis of $PbMnO_3$and $PbMnO_3$:Al_2O_3 shoes agglomeration whereas $PbMnO_3$:SiO_2 gives rod like morphology. The EDAX analysis confirms the formation of $PbMnO_3$, $PbMnO_3$: $SiO_2$and $PbMnO_3$:$Al_2O_3$with appropriate stoichiometry. SEM images along with EDAX analysis obtained for synthesizedthree nanocrystalline products are shown in Fig. 3a-c.TEM images along with SAED pattern obtained for synthesized three nanocrystalline products are shown in Fig. 4a-c. From Fig. 4a one can observe that most of the $PbMnO_3$crystals are cubic in nature. The particle size obtained by TEM for $PbMnO_3$ is found to be 187 nm. The particle size for $PbMnO_3$:$SiO_2$by TEM is 32.27 nm (Fig.4b). TEM analysis clearly reveals that crystals are cubic in nature and it well matches with XRD analysis. The particle size obtained for $PbMnO_3$:Al_2O_3 is 53.89 nm (Fig.4c). This figure shows that some of the crystals are big and hexagonal and most of them are cubic in nature. Surface area of material plays an important role in catalysis and gas sensing properties. In the present the typical N_2 adsorption/desorption isotherm and BJH pore distribution of prepared $PbMnO_3$, $PbMnO_3$:$SiO_2$and $PbMnO_3$:$Al_2O_3$are nearly same in curve shape which are depicted in Fig. 5a-c. This method (BET) leads to the identification of the isotherm profile as type IV in the BDDT system which is typical for mesoporous material. The BJH pore size distribution demonstrates that all the samples obtained have narrow pore diameter range. The BET surface area (S_{BET}), pore volume (Vp), pore diameter (Dp) and other parameters are recorded in Table 1. This clearly gives evidence that the doping and coating of metal ions with $PbMnO_3$ shows increase in large surface area (Table 1). A careful inspection of Table 1 shows that the surface area was found to be highest for $PbMnO_3$ is 187.9 cm^2/g, the average pore volume (Vp) and pore diameter (Dp) were 0.0657cc/g and 18.88 A^0 respectively. For $PbMnO_3$:$SiO_2$179.26 cm^2/g, the average pore volume (Vp) and pore diameter (Dp) were 0.0317 cc/g and 37.76A^0 respectively. For $PbMnO_3$:Al_2O_3 the BET surface area is 97.67 cm^2/g, the average pore volume (Vp) and pore diameter (Dp) were 0.0317 cc/g and 65.10A^0 respectively.

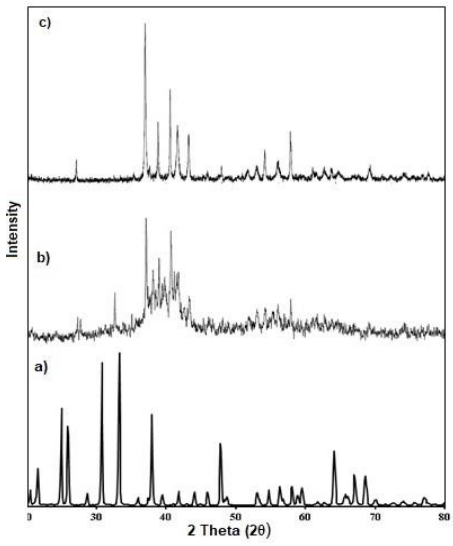
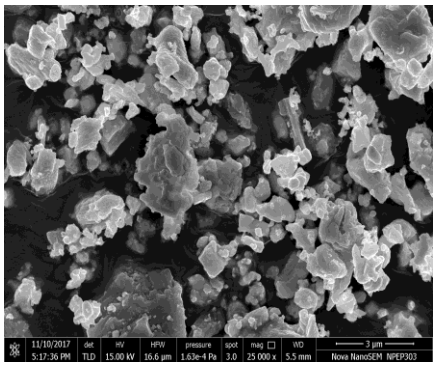
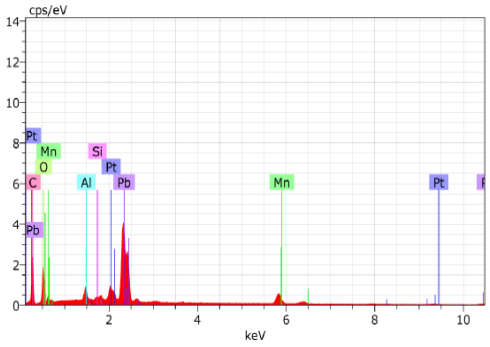
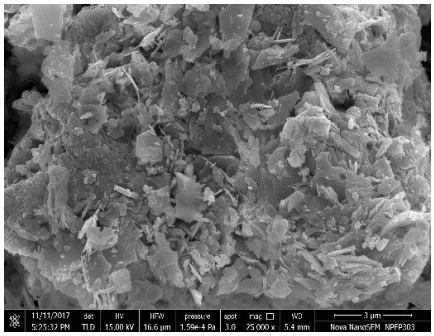
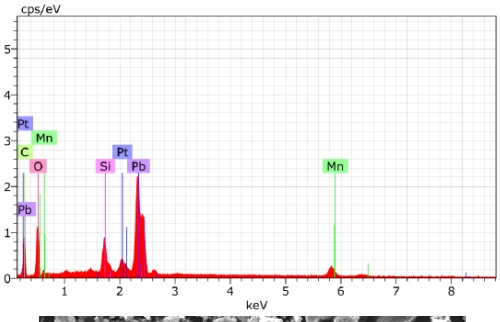


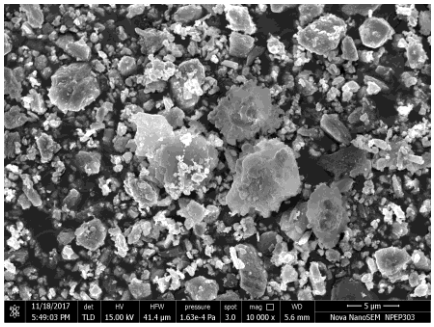
Fig.2: XRD analysis of (*a)* $PbMnO_3$, (*b*) $PbMnO_3$: SiO_2 and (*c*) $PbMnO_3$: Al_2O_3











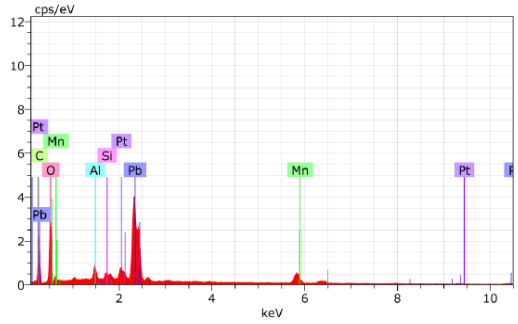
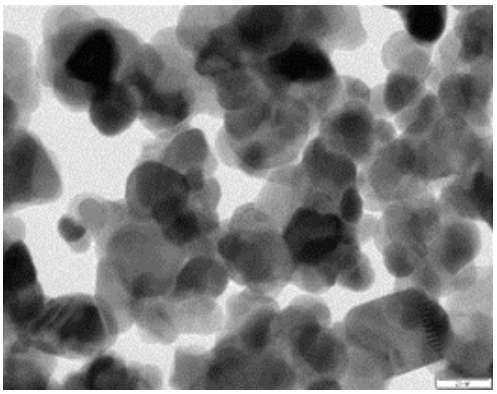
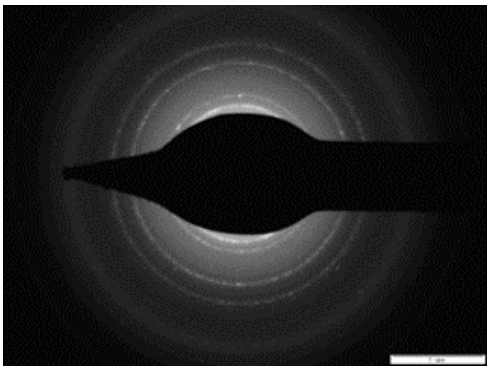
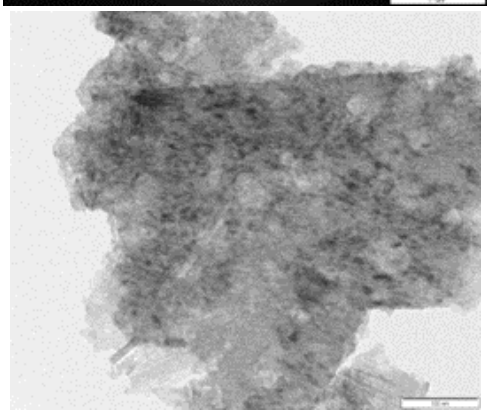


Fig. 3: SEM and EDAX analysis of a) $PbMnO_3$, b) $PbMnO_3$:SiO_2 and c) $PbMnO_3$:Al_2O_3.







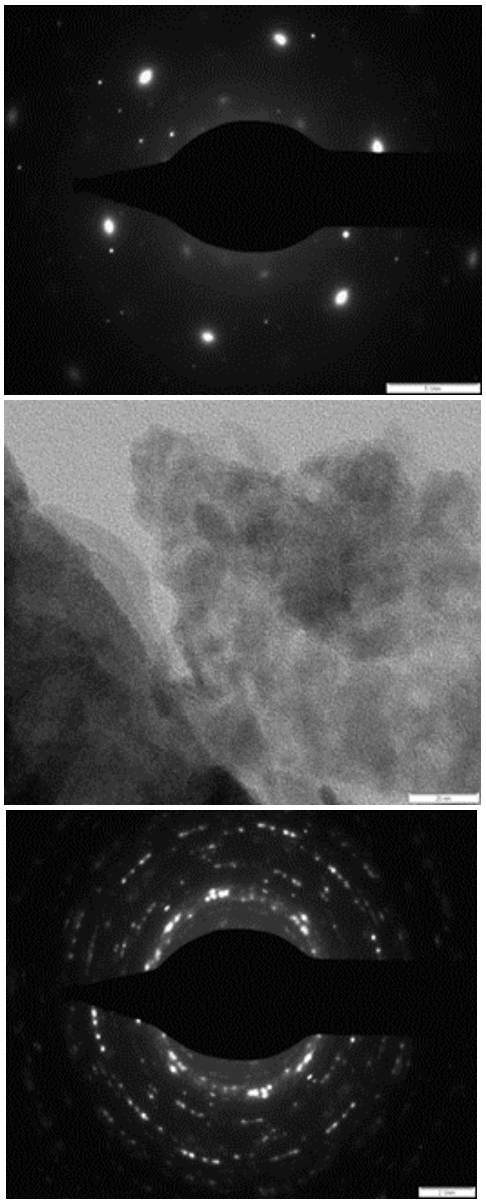


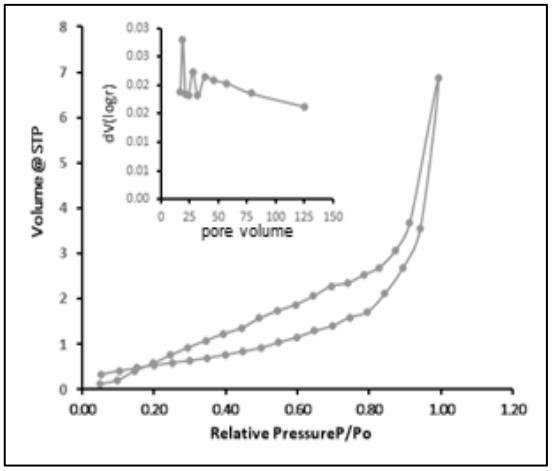
Fig. 4: TEM and SAED pattern of a) $PbMnO_3$, b) $PbMnO_3$:SiO_2 and c) $PbMnO_3$:Al_2O_3.

Table 1 : BET surface area, pore volume and pore diameter of $PbMnO_3$, $PbMnO_3$:$SiO_2$and $PbMnO_3$:Al_2O_3

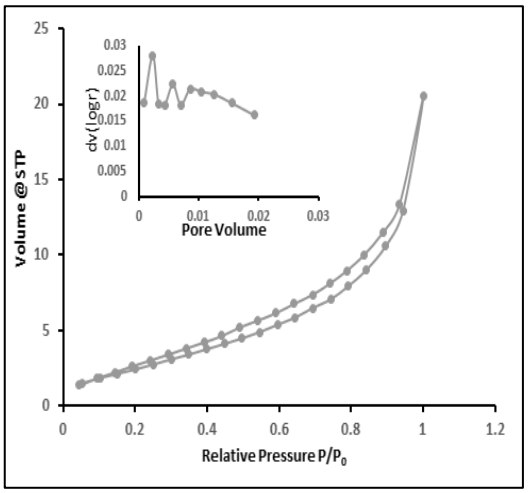
Synthesized compound	Surface area (m^2/g)	Pore volume (cc/g)	Pore diameter (Å)
$PbMnO_3$	187.9	0.0106	18.88
$PbMnO_3$: SiO_2	179.26	0.0317	65.10
$PbMnO_3$: Al_2O_3	97.67	0.0657	37.76

3.2 Selectivity of $PbMnO_3$, $PbMnO_3$: SiO_2 and $PbMnO_3$: Al_2O_3thick films for various gases:

Figure 5a-c depicts selectivity of sensing materials $PbMnO_3$ and modified $PbMnO_3$ towards various gases NH_3, H_2S, H_2, CO_2, CO and Cl_2. Figure 5a-c also shows the operating temperature change from 50 ^{0}C to 400 °C with 500 ppm of each gas. The results obtained reveals that the $PbMnO_3$ thick film gives maximum sensitivity to NH_3 (71.42) at temperature 200 °C. Further PbMnO3:Al_2O_3 gives highest sensitivity to H_2S (315.8) at 250 °C But $PbMnO_3$:SiO_2clearly shows this thick film act as aNH_3 gas sensor with highest sensitivity 1740 at temperature 50 ^{0}C as compared to $PbMnO_3$:Al_2O_3 and $PbMnO_3$ (Fig. 5c). This study clearly reveals that as the $PbMnO_3$modified it response to different gases.



(a)



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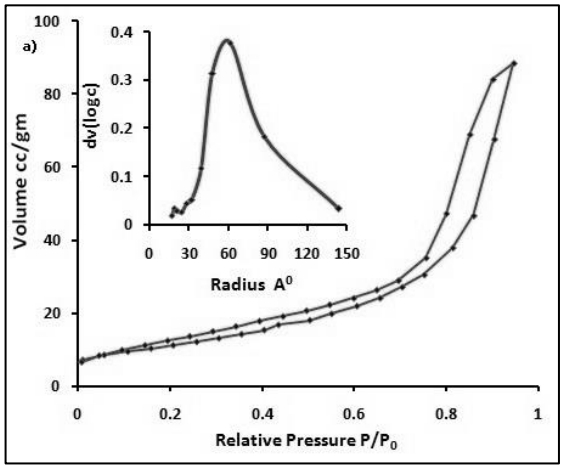


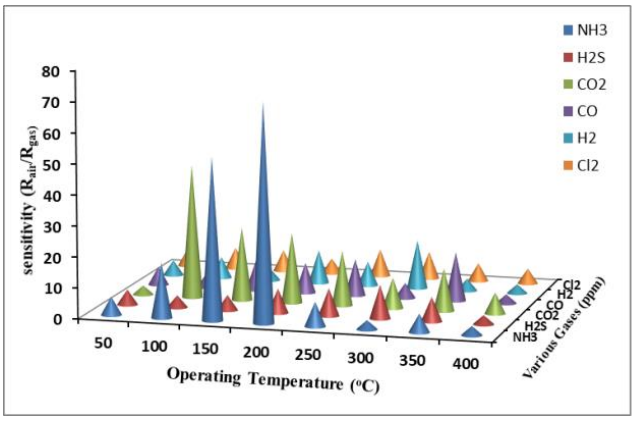
(c)

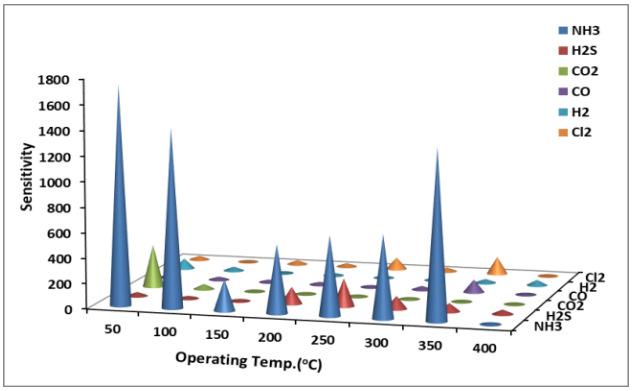
Fig. 5 : BET analysis of (a) $PbMnO_3$, (b) $PbMnO_3$:SiO_2 and (c) $PbMnO_3$:Al_2O_3.

3.3 Selectivity of $PbMnO_3$, $PbMnO_3$: SiO_2 and $PbMnO_3$: Al_2O_3 for $NH_3$and H_2S gas with various operating temperature:x

A particular sensing material shows highest gas response for a particular gas at a particular temperature. Using this method specific gas may be sensed by setting the temperature. Various gases show different energies for adsorption reaction on the metal oxide surface and hence response at various temperature depends on the gas being sensed. In the present investigation effect of annealing temperature 250 °C-450 °C on the sensitivity of $PbMnO_3$, $PbMnO_3$:$SiO_2$and $PbMnO_3$:Al_2O_3 on 500 ppm of NH_3 and H_2S are carried out (Fig. 6a-c). For the sake of comparison NH_3 gas sensing property of $PbMnO_3$, $PbMnO_3$: $SiO_2$and H_2S for $PbMnO_3$: Al_2O_3 thick films at different temperatures were also studied under identical annealing condition of temperature. Fabrication of sensors for gas sensing material is mainly depending upon annealing temperature. The sensing material must be annealed at various temperatures to obtain crystallization and structure determination. Because degree of crystalinity is important to attain the desired electronic properties which are prime importance for gas sensor application. In the present study the dependence of sensitivity of the synthesized $PbMnO_3$ at 500 ppm for NH_3, $PbMnO_3$:Al_2O_3 for H_2S and $PbMnO_3$:SiO_2 for NH_3 at annealing temperature of 250, 300, 350, 400 and 450 °C along with the operating temperature is visualized.

It was observed that the annealing in air renders more oxygen vacancy generation which increases H_2S gas sensing for $PbMnO_3$:Al_2O_3 and NH_3 gas sensing for $PbMnO_3$ and $PbMnO_3$:SiO_2. Further the keen observation of Fig. 6a-c shows that the sensitivity increases from 50 °C to 200 °C and later it decreases with further increase in the operating temperature. The maximum sensitivity was found to NH_3gas for $PbMnO_3$:SiO_2 thick film is 1740, $PbMnO_3$ thick film shows 71.42 to NH_3 gas and $PbMnO_3$:Al_2O_3 shows 315.8 for H_2S at annealing temperature 50 °C, 200 and 250 °C for 500 ppm each gas respectively.





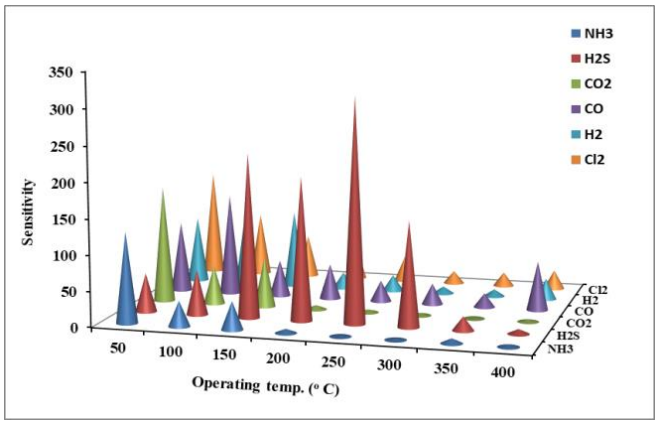


Fig. 6. Sensitivity of various gases at various temperatures on gas response for (a) $PbMnO_3$, (b) $PbMnO_3$:SiO_2 and (c) $PbMnO_3$:Al_2O_3.

3.4 Variation in sensitivity with gas concentration:

The dependence of sensitivity of $PbMnO_3$, $PbMnO_3$:$SiO_2$and $PbMnO_3$:Al_2O_3on the NH_3 and H_2S gas concentration at an operating temperature 50°C and is presented in Fig. 7a–c. It is observed that the sensitivity increases substantially in all three sensors prepared. In case of these three catalysts the gas concentration varied from 200 to 1000 ppm and then decreases with further increase in all three gas concentration. This linearity between gas concentration and sensitivity with lower concentration may be attributed to the availability of sufficient number of sensing sites on the film to act uponNH_3. Lowering in concentration shows that the surface coverage of gas molecules and hence less surface reaction between the surfaces adsorbed oxygen species and the gas molecules. With increase in the gas concentration increases the surface reaction due to a large surface coverage. In the present study the maximum sensitivity was obtained at an operating temperature 50 °C for the exposure of 1000 ppm of NH_3 gas.

The obtained linearity of thick film sensitivity in the low NH_3 concentration range (200-1000 ppm) suggests that the $PbMnO_3$, $PbMnO_3$:$SiO_2$and $PbMnO_3$:Al_2O_3can be properly applied to monitor the concentration ofNH_3 over the range studied.

3.5 Sensitivity mechanism of $PbMnO_3$:SiO_2thick film as NH_3 gas sensor:

The surface of $PbMnO_3$:SiO_2 adsorbs atmospheric oxygen molecule in the form of O^- or O^{2-} and hence conductivity decreases. These oxygen molecules takes electron from $PbMnO_3$:SiO_2 in the form of adsorbed $O^-_{PbMnO3:SiO2}$. The process occurs in the form of $O_{2(g)} + 2e- \rightarrow 2O^-_{PbMnO3:SiO2}$

Then $PbMnO_3$:SiO_2 becomes oxygen deficient. In the present study when reducing gas NH_3 reacts with negatively charged oxygen adsorbate then the trapped electrons are given back to conduction band of $PbMnO_3$:SiO_2. The adsorbed ammonia gets decomposed releasing some energy ease of this electron jump into the conduction band of $PbMnO_3$:SiO_2giving increase in the conductivity of the sensor. Hence the possible mechanism proposed for $PbMnO_3$:SiO2towards NH_3 is,

$2NH_3 + 3O^-_{PbMnO3:SiO2} \rightarrow 3H_2O + N_2 + 3e^-$ OR
$4NH_3 + 3O^-_{PbMnO3:SiO2} \rightarrow 6H_2O + 2N_2 + 6e^-$

Increase in operating temperature increases the thermal energy causing oxidation of NH_3 and hence NH_3 donates electrons to PbMnO3:SiO2. This confirms gas response rises with an operating temperature due to decrease in resistance. The maximum values of sensitivity indicate this is the actual energy needed to proceed the reaction. But at very high temperature desorption takes place because oxygen adsorbates are desorbed from the surface of the sensor [22].

3.6 Sensitivity mechanism of $PbMnO_3$ and $PbMnO_3$: SiO_2 thick films to NH_3 gas sensor:

The $PbMnO_3$:SiO_2 thick film was surface modified by coating SiO_2 particles were distributed homogeneously on the surface of the $PbMnO_3$:SiO_2. The coating of SiO_2 enhance the catalytic reaction efficiently and the overall change in resistance on exposure of reducing gas (NH_3) leads to rise in

sensitivity. The thick film gas sensing mechanism of $PbMnO_3$:SiO_2 is mainly based on surface modification of material synthesized. The sensing material adsorbs molecular oxygen from air and gets dissociated to various species like O^-, $O^{2-}$and O^{2-}. The O^{2-}adsorbed oxygen ions on surface of sensing material and the oxide particles form a depletion layer. This depletion layer creates an electric field between adsorbed oxygen species and the metal oxide species. At definite temperature NH_3 gas can be oxidized into NO_2^- by reacting with adsorbed oxygen. The nitroxide formed diminishes when it is exposed to oxidizing conditions [23]. When gas response is measured during high temperature, the desorption of gas leads to the sensitivity of the material. The sensitivity of these oxygen species mainly depends on the operating temperature [24]. When the thick film of $PbMnO_3$ and $PbMnO_3$:$SiO_2$was fully exposed to NH_3 gas then the species O^- reacts with NH_3 gas and extracts the electrons from the conduction band of the n-type $PbMnO_3$ thick film. This shows that the amount of number of electrons on the surface of $PbMnO_3$:SiO_2 decreases and hence the film resistance as found to be increase.

3.7 Gas Response and Recovery

The response and recovery time for the most sensitive $PbMnO_3$: SiO_2 during a week are represented in Fig. 7. The gas response for $NH_3$with concentration 100 ppm at 50 °C was quick (4 s) and recovery time was 22 s. These results showed that the sensors have an excellent stability towards the NH_3 gas. There is no baseline shifting. The gas sensing response and recovery times are important parameters to evaluate the performance of a gas sensor.

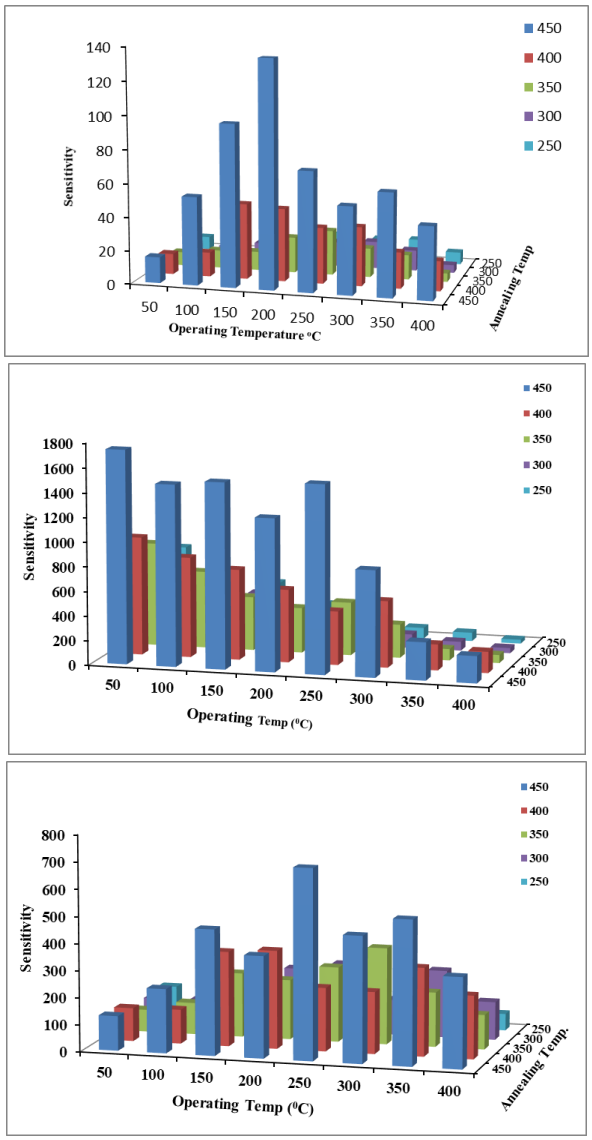


Fig. 7. Effect of annealing temperatures operating for a) $PbMnO_3$ for NH_3 gas, b) $PbMnO_3$:SiO_2 for NH_3 gas and c) $PbMnO_3$:Al_2O_3 for H_2S gas

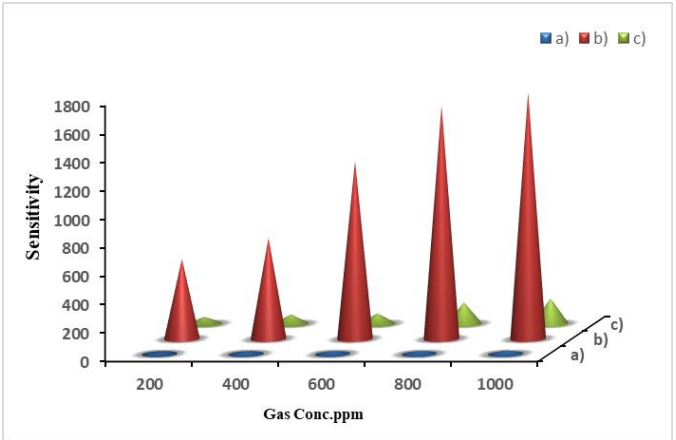


Fig. 8. Effect of NH_3 gas concentration on sensitivity (a) $PbMnO_3$, (b) $PbMnO_3$:SiO_2 and (c) $PbMnO_3$:Al_2O_3

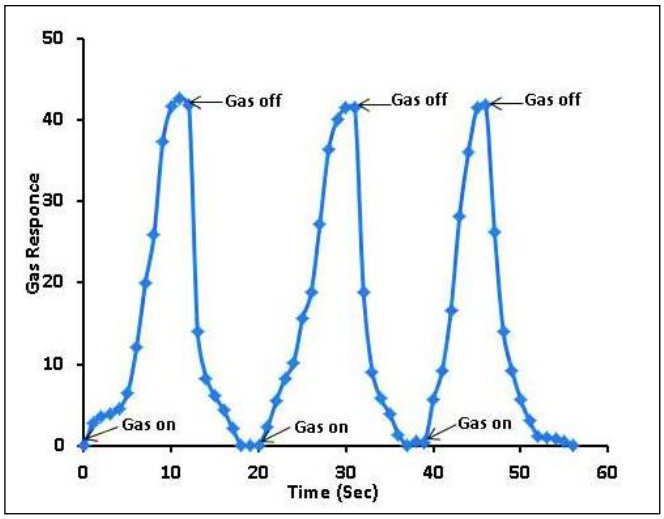


Fig. 9: Gas response and gas recovery of NH_3 gas with$PbMnO_3$:SiO_2 catalyst.

IV. CONCLUSION

Nanocrystalline $PbMnO_3$ and modified $PbMnO_3$ are successfully prepared by mechanochemical and hydrothermal method. The thick film for these materials was prepared by screen printing method. The prepared thick films were applied for sensing of different gases. Following important conclusions were drawn from the present study

1. The unmodified $PbMnO_3$ thick film was found to be NH_3 sensitive at 200 °C.
2. $PbMnO_3$:SiO_2 sensor is selective to NH_3 gas and forbidden the response to other gases.
3. $PbMnO_3$: Al_2O_3 sensor is found to be highly sensitive to H_2S gas.
4. Gas sensing mechanism for each gas with sensing material was established successfully.
5. Modification of $PbMnO_3$alters the gas sensing properties.

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