# Thick Films of LaNiO$_3$ Perovskite Structure Impregnated with In and Bi Oxides as Acetonitrile Sensor

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## Abstract

Thick films of LaNiO$_3$ having perovskite structure impregnated with indium and bismuth oxides have been used as sensing material for acetonitrile (CH$_3$CN) gas. The sensor response for CH$_3$CN is quite good with an excellent recovery for partial pressure from 3 ppm to 20 ppm between 200 and 250°C. LaNiO$_3$ alone has exhibited low response, but after impregnation of In$_2$O$_3$ and Bi$_2$O$_3$ have given increased sensitivity even with 3 ppm partial pressure of CH$_3$CN at 200°C. It is assumed that CH$_3$CN is undergoing oxidation reaction on surface of the film.

**Key Words :** LaNiO$_3$, LaNiO$_3$-In$_2$O$_3$, LaNiO$_3$-Bi$_2$O$_3$, CH$_3$CN detection

## 1. Introduction

Perovskites are thermally stable compounds, exhibiting variety of novel properties such as magnetic materials, semi-conductors, conductors, gas sensors and also these are quite resistant to poisoning. LaNiO$_3$ has been tested as a catalyst for a few oxidation reactions and also in some gas sensor property[1]. LaNiO$_3$ adsorbs gases selectively changing electronic property such as resistance and therefore, can be employed as a gas sensing material device. CH$_3$CN is widely used as an industrial solvent and in chemical intermediates. It is well known toxic as it attacks the liver and blood, leading to many physiological problems. Therefore, early detection of CH$_3$CN is very important to prevent health hazards.

Xuchen et al.[1] investigated sensitivity and response characteristics of the lanthanum nickelate in the exhaust gases of air-propane combustion. Mohan et al.[2] reported that LaNiO$_3$ is a p-type with high conductivity at room temperature and its conductivity decrease with a decrease in Ni$^{+3}$ concentration.

In the present investigation, we prepared LaNiO$_3$ perovskite by chemical co-precipitation technique. Metal oxides such as In$_2$O$_3$ and Bi$_2$O$_3$ were impregnated in LaNiO$_3$ taking 2% of metal by weight employing chemical wet impregnation method. Sensing property to CH$_3$CN gas was studied over the thick films of these mixed oxides at different partial pressures at varying temperatures.

## 2. Experimental

Nitrate of lanthanum and nickel (AR grade) were taken in stoichiometric molar quantities and dissolved in distilled water. Sodium hydroxide solution (10%) was added drop wise till the precipitation of metal hydroxides (pH 9 – 10) was completed. The precipitate was agglomerated on a steam bath for 3 – 4 h and then 5 ml hydrogen peroxide was added drop wise with constant stirring. The precipitate was filtered, washed several times with distilled water, dried and fired at 700°C for 10 – 15 h in air. This material was characterized by powder X-ray diffraction technique.

Wet impregnation of In$_2$O$_3$ and Bi$_2$O$_3$ were carried out taking 2% by weight of the metal (In and Bi) in the LaNiO$_3$ perovskite. These compounds are designated as LaNiO$_3$-In$_2$O$_3$ and LaNiO$_3$-Bi$_2$O$_3$ respectively. A calculated weight of indium or bismuth nitrate was dissolved in distilled water in a beaker and to this solution calculated weight of LaNiO$_3$ powder was added. The mixture solution was stirred continuously on magnetic stirrer. After several hours of stirring the sample was slowly

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heated to dryness with constant stirring. The dried sample was heated at 500°C for 4 h in air.

The surface morphologies of the films prepared over silica substrate were examined by scanning electron microscope (SEM ABT DS130C) after gold metallization at 2 mA for 5 minutes.

These compounds were tested as gas sensing materials as devices by preparing thick films employing screen printing technique. The sensing materials were deposited on alumina substrate $(0.7 \times 1 \text{ cm}^2)$ which contains a heating element on the back side of the substrate. The detailed procedure is given elsewhere[3,4]. After depositing the films, they were dried at 110°C for 24 h followed by firing at 600°C for 1 h and then ageing at 400°C for 72 h. Before testing the sensing property, the resistances of the films were recorded at different temperatures. The sensors were connected with the long bonding pins for electrical conduction and they were mounted on a printed circuit board. The characteristics of the sensor were tested in a testing steel chamber after injecting test gas under study in a continuous flow of synthetic air at different temperatures. The sensor signals were fed to a test system monitored by a PC.

## 3. Results and Discussion

LaNiO$_3$ was prepared by chemical co-precipitation method and characterized by employing X-ray diffraction technique using Cu K$\alpha$ target filtered through Ni. The $d_{hkl}$ and relative intensities were in good agreement with those reported in JCPDS file.

Fig. 1 shows the sensor response in air against time as a representative plot for the different partial pressure of CH$_3$CN on LaNiO$_3$ and impregnated metal oxide



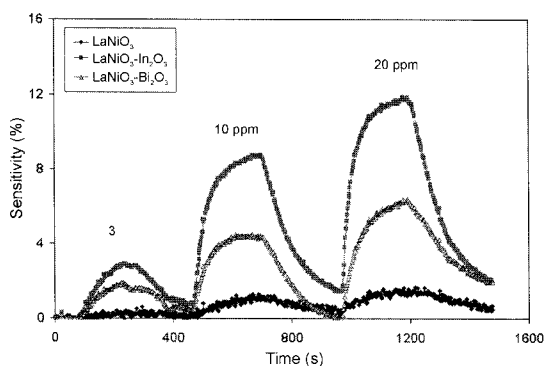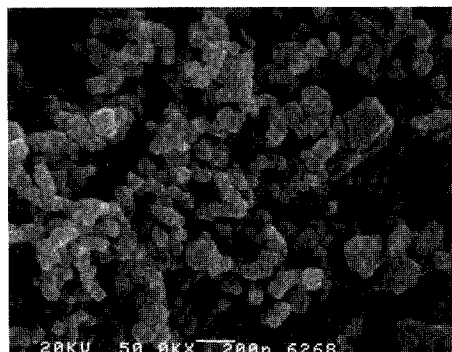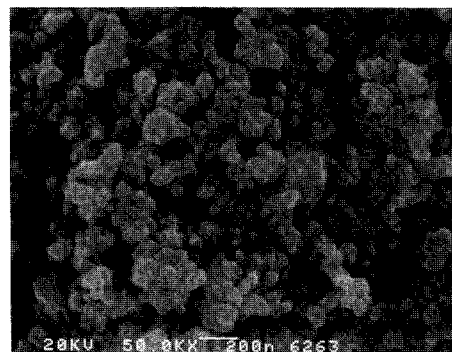Fig. 1. The sensor response to CH$_3$CN at 250°C.


(a)


(b)

Fig. 2. Scanning electron micrographs of (a) LaNiO$_3$ and (b) LaNiO$_3$-In$_2$O$_3$ thick films.

devices at 250°C. The sensitivity increases with increase in partial pressure of CH$_3$CN. The test gas was injected for five minutes and allowing three minutes for the recovery of the device before next injection. These devices gave prominent signals of CH$_3$CN detection without noise, but LaNiO$_3$ showed low sensitivity. The device had good response time and also fast recovery once CH$_3$CN is removed from the stream gas.

Fig. 2 shows the scanning electron micrographs indicating surface morphology of (a) LaNiO$_3$ and (b) LaNiO$_3$-In$_2$O$_3$. It is clear that surface morphology has changed after impregnation of In$_2$O$_3$ in LaNiO$_3$. Impregnation leads to agglomeration of particles with more porosity and increasing surface defects to increase more active sites for adsorption and increasing sensor response. The micrographs show the porous crystalline structure with wide distribution of grain sizes ranging from 60 to 150 nm.

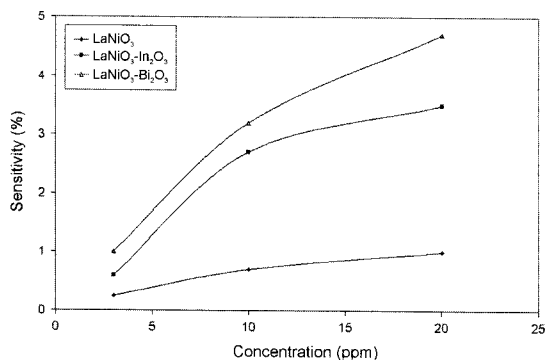Figs. 3 and 4 represent sensor response with partial pressure of CH$_3$CN on different devices at 250 and

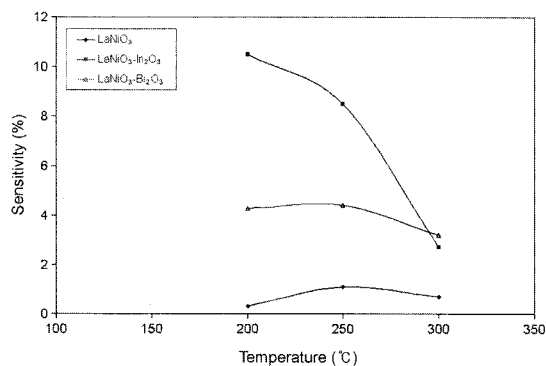Fig. 3. Sensitivity with respect to concentration at 250°C.



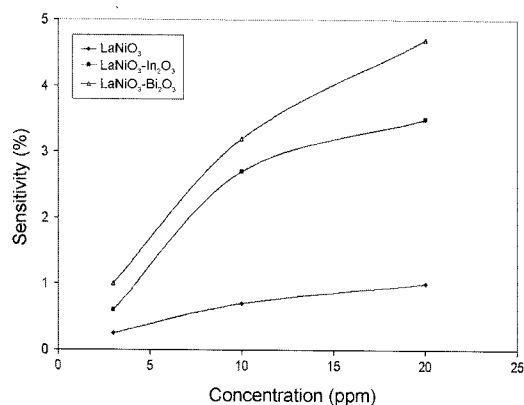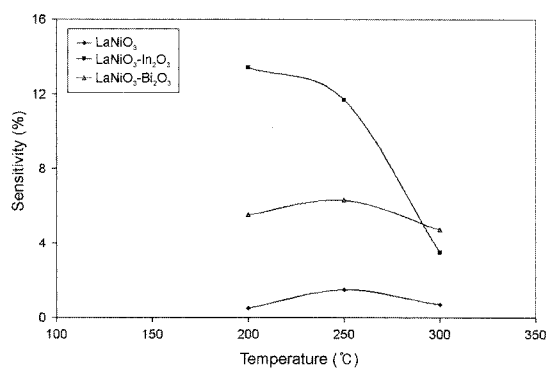Fig. 4. Sensitivity with respect to concentration at 300°C.



Fig. 5. Sensitivity against temperature at 10 ppm CH$_3$CN.



Fig. 6. Sensitivity against temperature at 20 ppm CH$_3$CN.

300°C respectively. As the partial pressure increases sensor response increases but the increase is not linear. At 200 and 250°C LaNiO$_3$-In$_2$O$_3$ gave higher response followed by LaNiO$_3$-Bi$_2$O$_3$ but at 300°C LaNiO$_3$-Bi$_2$O$_3$ gave marginally better response than others whereas LaNiO$_3$ showed poor response. Increase in sensitivity by incorporation of In$_2$O$_3$ and Bi$_2$O$_3$ might have created more active sites on the surface of LaNiO$_3$ which resulted in more adsorption of CH$_3$CN than LaNiO$_3$ alone.

Fig. 5 depicts the change in sensor response as a function of temperatures on different devices at a partial pressure of 10 ppm. LaNiO$_3$-In$_2$O$_3$ showed good sensor response at 200°C but the sensitivity decreases with the temperatures, whereas LaNiO$_3$ and LaNiO$_3$-Bi$_2$O$_3$ sensitivities increase from 200 to 250°C and then at higher temperatures fall in sensitivities.

Fig. 6 shows the sensor response as a function of temperature at the partial pressure of 20 ppm CH$_3$CN. The trend is similar to that of 10 ppm CH$_3$CN partial pres-

Table 1. Resistance of different sensors at various temperatures and corresponding percentage sensitivities for 20 ppm of CH$_3$CN at that temperatures

| Temperature (°C) | 19(r.t.) | 200 | 250 | 300 |
|---|---|---|---|---|
| LaNiO$_3$ R(Ω) | 69 | 65 | 63 | 61 |
| LaNiO$_3$ S(%) | | 0.5 | 1.5 | 1.0 |
| LaNiO$_3$-In$_2$O$_3$ R(Ω) | 369 | 248 | 234 | 198 |
| LaNiO$_3$-In$_2$O$_3$ S(%) | | 13.4 | 11.7 | 3.5 |
| LaNiO$_3$-Bi$_2$O$_3$ R(Ω) | 831 | 361 | 304 | 298 |
| LaNiO$_3$-Bi$_2$O$_3$ S(%) | | 5.5 | 6.3 | 4.7 |

sure. In$_2$O$_3$ is well known catalyst for several oxidation reactions and therefore, favouring sensitive response with CH$_3$CN. However, it is not very active beyond 250°C.

The resistances of different sensors at the sensing temperatures are shown in Table 1. It has been observed that the change in resistance of LaNiO$_3$ is very small with temperatures, whereas changes in resistance in LaNiO$_3$-In$_2$O$_3$ and LaNiO$_3$-Bi$_2$O$_3$ are significant indi-

cating better semi-conducting properties. In our view, the resistance is not the only criteria for better sensing property, as it is seen that $LaNiO_3$-$Bi_2O_3$ in spite of higher resistance than $LaNiO_3$-$In_2O_3$ showed lower sensitivity. Besides resistance there are other factors which influence the sensor response such as active sites, surface morphology or structure, metal oxidation states and surface defects.

Park et al.[5] reported a high sensitivity to $CH_3CN$ on Pd doped $SnO_2$ sensors and they found that $CH_3CN$ decomposes at 130°C producing $H_2O$, $NH_3$, $CO_2$, and $N_2O$ as products. They concluded that the oxidation reaction was dominant for $SnO_2$ based sensor. It is presumed that $CH_3CN$ adsorbs on the surface of the sensor, reacts with the available oxygen on the surface to get $CO_2$ and ammonia as the oxidation products. Ammonia may further be oxidized to give products as $N_2O$ and $H_2O$. $LaNiO_3$ is a slightly oxygen deficient compound and perhaps it is difficult to remove the surface lattice oxygen for the oxidation reaction. When $In_2O_3$ is impregnated in $LaNiO_3$ activity is increased considerably, probably $In_2O_3$ can easily furnish its lattice oxygen for the participation in the reaction. Ivanovskaya et al.[6] had also reported that the high response of $In_2O_3$ to reducing gas at high temperature is due to its donation of lattice oxygen.

## 4. Conclusion

Thick films of $In_2O_3$ and $Bi_2O_3$ impregnated in $LaNiO_3$ have been developed for sensing the toxic gas $CH_3CN$. These fabricated devices have been tested as gas sensors for the concentration range between 3 to 20 ppm and at 200 to 300°C. $LaNiO_3$-$In_2O_3$ gave better sensor response than others, may be due to the participation of lattice oxygen for $CH_3CN$ oxidation and creating more adsorption sites on the surface. The devices showed good sensor response as well as good recovery

after switching off the test gas. $LaNiO_3$-$In_2O_3$ looks to be more promising and efficient $CH_3CN$ gas sensor material than others at 200 and 250°C.

## Acknowledgement

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