Influence of Humidity on the NO_2 Sensing Properties of $SrCo_{0.1}Ti_{0.9}O_3$

Neha Sarin, Sachin Kumar, Ivan P. Parkin and Vandna Luthra

Abstract Strontium Cobalt Titanate (SCT) was synthesized via solid state route. Phase formation was analyzed using X-ray diffraction (XRD) technique. Resistive sensors were made using screen printing technique and corresponding sensing properties were investigated in dry as well as humid environment (RH 50%). Experimental results demonstrated that sensors displayed least humidity interference at 400 °C. The operating temperature of the sensor was optimized for best responsiveness. These type of sensors can be effectively used in environmental monitoring of NO_2 gas at low ppm.

136.1 Introduction

Nitrogen oxides emissions are responsible for pulmonary disease and even damages to the human immunity system. Nitrogen oxides (NO_x) are produced by petrol and diesel burning engines is a poisonous, odorless, colorless gas. Once mixed with air it quickly combines to form NO_2 which is highly toxic gas, pungent smelling gas and a major component of outdoor pollution [1]. Nitrogen dioxide is toxic on inhalation; it can be easily identified by smell. However, one complex feature of this is that exposure to the gas at low concentration anaesthetizes the nose causing the likelihood that increased concentrations in an environment may go undetected, creating potential health risks. The main risks of nitrogen dioxide are their effect on

N. Sarin · S. Kumar · V. Luthra (✉)
Department of Physics, Gargi College, Siri Fort Road,
New Delhi 110049, India
e-mail: vandna_arora@yahoo.com

N. Sarin · S. Kumar
Department of Physics & Astrophysics, University of Delhi,
New Delhi 110007, Delhi, India

I. P. Parkin
Department of Chemistry, University College London,
20 Gordon Street, London WC1H 0AJ, UK

the lungs. People with bronchitis or asthma are predominantly sensitive to the gas, and lungs may become inflamed, leading to breathing difficulties. According to international air quality standards, long-term exposure to low concentration of NO_2 is harmful. The need for air quality control demands a sensor selective to NO_x as well as with ability to detect at low concentrations.

Humidity poses a great challenge in the metal oxide based gas sensors. In numerous cases, increase of humidity in the atmosphere to a great extent impedes the response of sensor [2]. Humidity is a common cross-contaminant that can vary widely in concentration with changes in ambient conditions. The effects of humidity on NO_2 detection need quantification and must be kept under control.

A variety of n-type materials have investigated for gas sensing measurements in contrast to p-type materials that offer advantage over n-type materials like reduced cross sensitivity, lower humidity interference, promote selective oxidation of volatile organic compounds [3]. The distinctive oxygen adsorption of p-type materials maybe used to design high-performance gas sensors that show low humidity dependence and rapid recovery kinetics [4, 5].

Moreover, a wide variety of materials have been studied and used as sensing elements for NO_2 detection [6]. Among them, ABO_3 type perovskite has received considerable attention due to admirable gas sensitivity, tolerance towards higher doping levels and stability over a wide temperature range [7, 8]. This doping flexibility allows control of various properties such as sensitivity and selectivity. Strontium Titanate ($SrTiO_3$) is an n-type perovskite which in its pure state has rather low conductivity. However, its conductivity can be enhanced by acceptor doping at Ti-site. Also acceptor doping of trivalent ions on the quadrivalent ions induce p-type conduction [9]. In the present report, $SrCo_{0.1}Ti_{0.9}O_3$ was prepared by solid state route. Its NO_2 sensing properties has been tested in dry as well as humid environments at various operating temperatures.

136.2 Experimental

$SrCo_{0.1}Ti_{0.9}O_3$ was prepared using solid state reaction method. The powder was then calcined at 1100 °C for 3 h. The phase formation was investigated via X-ray diffractometer (Bruker, D8 advanced diffractometer, Germany) using CuK_α ($\lambda = 1.541$ Å) radiation, where the patterns were collected over a range of 10°–80° with a scan rate of 2°/min.

The sensor was fabricated onto 3×3 mm^2 alumina substrates containing laser etched interdigitated gold electrodes for resistance measurements on the upper layer with electrode gap ~ 0.15 mm. A platinum heater track housed at the bottom of the tile was used to achieve the desired temperature. (Courtesy: City Technology). Ink for screen printing was prepared by mixing the powder with organic vehicle (ESL-400, Agmet Ltd.) and grinding in a mortar and pestle till a homogeneous

suspension was obtained. Resulting ink was then screen printed using DEK1202 screen printer. After each print, the layer was dried under an infra-red lamp for 20 min. A total of 5 layers were deposited. Afterward, sensor was fired at 600 °C for an hour in an Elite Thermal Systems BRF15 furnace to evaporate the organic vehicle The sensors were then bound onto the brass pins in standard polysulphide housing.

The sensor were investigated in both dry air as well as 50% RH with NO_2 as test gas at 350, 400 and 500 °C as operating temperatures.

136.3 Result and Discussion

XRD pattern is indicative of the crystalline nature (Fig. 136.1). The samples in perovskite phase with cubic structure were indexed to JCPDS card #86-0177 and no additional peaks were observed indicating Co has is dissolved in the structure and no secondary phase is detected.

The sensitivity of sensors is measured as a function of their baseline resistance in air (Ro). For reducing gases, the response is Ro/Rg, where Rg is the resistance of the sensor during the test gas pulse. For oxidising gases, the response is the reciprocal of response in reducing gas (Rg/Ro). Figure 136.2. shows the gas sensing response of Co-doped $SrTiO_3$ to NO_2 at 400 °C at 50 ppm. Sensor demonstrated a maximum sensing response of 2.93 at an operating temperature of 400 °C whereas in presence of humidity it displayed a response 2.6. It can be observed from Fig. 136.3, that the response increases with increase in concentration which may be due to larger availability of test gas in the atmosphere surrounding

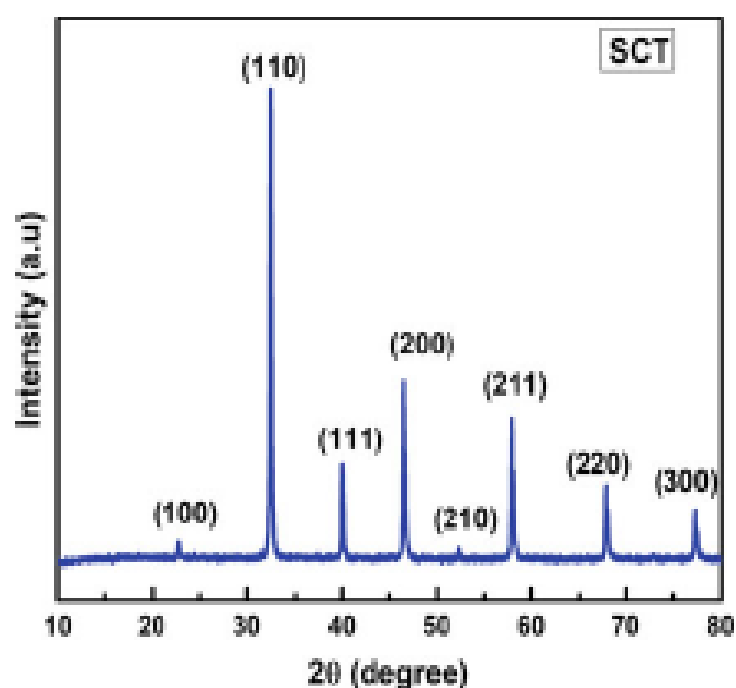Fig. 136.1 The X-ray diffraction pattern of $SrCo_{0.1}Ti_{0.9}O_3$

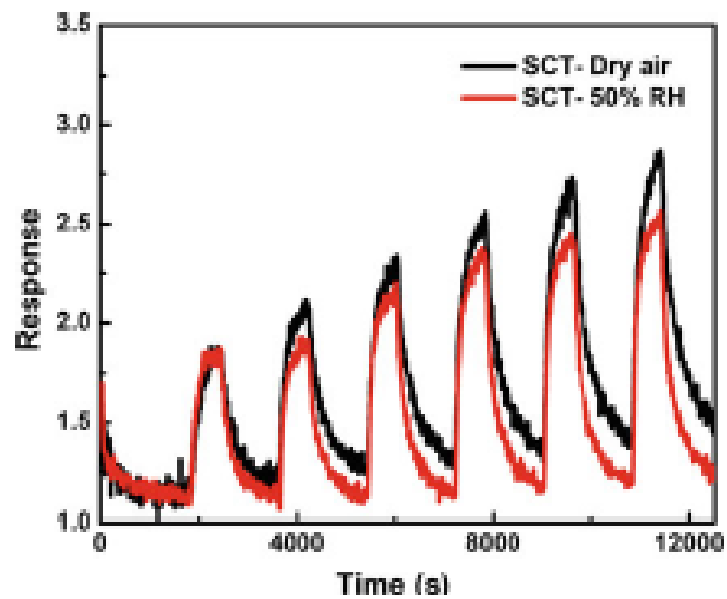**Fig. 136.2** Gas sensing response of $SrCo_{0.1}T_{0.9}O_3$ in dry air and 50% RH (5–50 ppm)
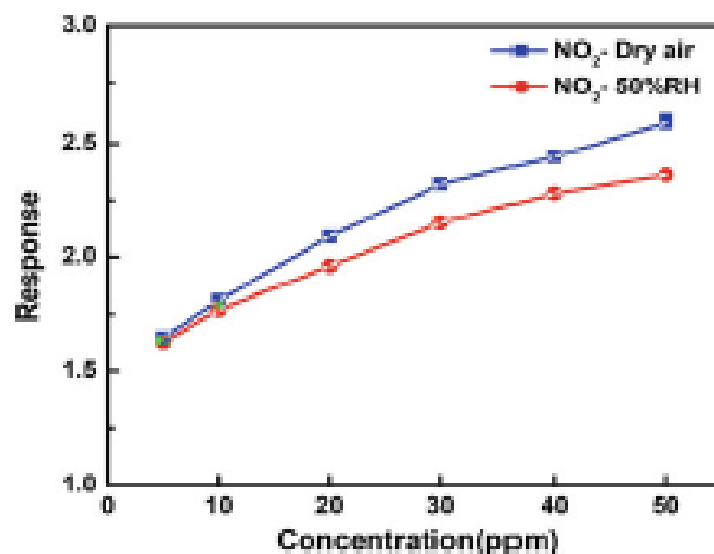

Fig. 136.3 Response of pure and doped samples at concentrations between 5 and 50 ppm to a 600 s exposure to ethanol gas at 400 °C

the sensor. However, it is noticeable from Fig. 136.3 that gas response in dry air at various concentrations is only slightly larger than response in humid air. The response to NO_2 at temperature 400 °C is seen to be higher than the response observed at 500 °C, however, the resistance of the sensors was very high at 350 °C (Table 136.1). Moreover, least humidity inference is observed for sensor at 400 °C. The sensor demonstrated promising gas sensing response and ~7 to 9% (within the limits of error) diminished response in humid environment as compared to dry air towards NO_2 at 400 °C at 50 ppm (Fig. 136.2).

Table 136.1 Sensor response at various temperatures to NO_2 at 50 ppm in dry air as well as 50% RH

S. No	Temperature (°C)	Response—dry air	Response—50% RH	Humidity interference
1.	350	High resistance	High resistance	–
2.	400	2.93	2.6	7–9%
3.	500	2.1	1.81	15–17%

136.3.1 Gas Sensing Mechanism

Semi-conducting metal oxides exhibit a change in conductivity due to adsorption or desorption of gas molecules. This change in the conductivity helps us to get information about the gas response signal [10, 11]. Oxygen species are adsorbed onto the surface, forming $O_{(ads)}^-$ species and remove electrons from the bulk of the material, this leads to the formation of a depletion region. In the presence of a test gas, oxygen is removed from the surface, reintroducing trapped electrons into the material, decreasing the size of the depletion region and increasing the conductivity. For an n-type material resistance increases due to electron capture in presence of oxidizing gas whereas for p-type material resistance decreases. The decrease in resistance of p-type material upon exposure to oxidizing gases can be explained by the increase of hole concentration in the shell layer due to the ionosorption of oxidizing gas.

The study of sensors in a humid environment is imperative, to test their reliability in actual atmospheric conditions. In wet atmosphere, ratio of water molecules to active sites (metal in metal oxide) decides the adsorption mechanism. Chemisorption mechanism is followed at low humidity level while physisorption is observed at higher levels of humidity. The increase in conductivity with increasing RH is mainly due to the increase of the charge carriers upon adsorption of water/gas vapors by the surface layer. The adsorbed water molecules get ionized on the surface and the hydronium (H_3O^+) ions are produced by the assistance of high electric charge density in the neighborhood of the hydroxyl (OH^-) sites resulting in enhancement of conduction to the adjacent sites. Thus, maintaining the gas sensing response in presence of humidity without substantial drop in parallel to the gas sensing response in dry air. Water-related conduction in ceramic and porous materials is known to mainly occur as a surface mechanism [12, 13]. A study of the variation of operating temperature on gas sensitivity in dry air and 50% RH in the present work shows least humidity interference and maximum sensitivity at 400 °C which is in agreement with the effects observed in other systems [14]. Such studies can be exploited for various applications.

136.4 Conclusion

Co-doped $SrTiO_3$ was synthesized, characterized and used to fabricate gas sensor. Sensor demonstrated a noticeable increase in responsiveness to NO_2 at 400 °C in comparison to other operating temperatures. Furthermore, the response at humid conditions was 7–9% lesser than observed in dry air. Consequently, these types of sensors can be effectively used in environmental monitoring of low ppm of NO_2 gas in dry as well as humid environment due to ease of production and low synthesis cost of materials.

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