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Experimental Investigations on Humidity-Sensing Behaviour of Neodymium Oxide

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In this paper, we report the humidity-sensing behaviour of neodymium oxide (99% pure, Johnson & Matthey, London). It was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and by measuring the mass loss. From SEM, the average particle size is 60–90 nm and particles have a random pore size. XRD reveals that at room temperature the sensing material is $Nd(OH)_3$ and is crystalline in nature. When neodymium oxide was annealed at 200°C and at higher temperatures, it became Nd_2O_3. The particle size calculated from Scherrer's formula varies from 100 to 110 nm. A pellet of this material was made using a hydraulic pressing machine (M.B. Instruments, New Delhi) for use as a sensing element after thermal annealing at temperatures of 200, 400, 600 and 800°C. After each step of annealing, the sensing element was placed in a specially designed conductivity holder and exposed to humidity inside a chamber with controlled humidity. Variations in resistance due to the adsorption of water vapour through the sensing element were observed. The sensitivity of the sensing element, the repeatability and the effect of temperature on morphology and sensing characteristics were studied.

1. Introduction

Humidity plays a very important role in the environment as well as in human life.[1–2] It adsorbs heat and an appropriate level of humidity is necessary for industrial processes. Manufactured products are packed in a low or moisture-free environment. Human discomfort occurs if the humidity level in the environment becomes either too low or too high. The measurement of humidity gives us an estimate of the amount of water vapour present in the air. Some of the reasons for the importance of humidity measurement[3–5] are listed below:

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1. In many production and manufacturing processes, the quality of the end product depends on controlling the humidity of the surrounding environment.
2. Human health, productivity and comfort are adversely affected by extremely humid conditions.
3. Humidity sensing and control are important in the optimal functioning of most home appliances.
4. Because of the discharge of electrostatic energy that accumulates in solid-state electronic equipment in a dry environment, humidity control is necessary to ensure the optimal functioning of instruments.

The increasing importance of measuring humidity has motivated researchers to search for more reliable and cost-effective humidity sensors and related control systems. There have been many approaches considered with the aim of developing a feasible humidity measurement technique.

Rare-earth oxides (REOs) have a tremendous range of applications in optics, solid-state electronics and transparent optoionic devices. They have high resistivity ($\rho \sim 10^{15}$ Ωcm), a high dielectric constant (ϵ = 7–20), a large band gap (4–6 eV) and a high recrystallization temperature. Nd_2O_3 is an REO that exhibits a hygroscopic property leading to the formation of hydroxides. This hygroscopic nature affects the electrical properties[6–9] of sensing materials.

2. Preparation of Sensing Element

Six hundred milligrams of neodymium oxide (99% pure, Johnson & Matthey, London) was used, and after vigorous grinding for 6 h, was mixed well with 10% glass powder. The addition of glass powder as a permanent binder during the process plays a major role in increasing the adhesiveness of the material, enabling the formation of a pellet. The pellet with 3 mm thickness and 9 mm diameter was made at a pressure 79 MPa using a hydraulic pressing machine (M.B. Instruments, New Delhi) at room temperature, and it was used as a sensing element. This prepared pellet was thermally annealed at temperatures of 200, 400, 600 and 800°C to study the effects of temperature on the morphology and sensing characteristics.

3. Material Characterization

3.1 *Scanning electron micrographs*

Figure 1 shows a scanning electron micrograph of the pellet at room temperature. Micropores can be seen in the photograph. The size of the particles varies from 60 to 90 nm. Figure 2(a) shows a micrograph of a pellet annealed at 200°C. Larger and random pores are observed for the pellet annealed at 400°C, as shown in Figs. 2(b) and 2(c).

3.2 *X-Ray diffraction*

Figure 3(a) shows XRD patterns of the neodymium oxide in powder form at room temperature. It reveals that the material consists of $Nd(OH)_3$ with a small amount of impurity. The XRD pattern of the sensing material annealed at 400°C is shown in

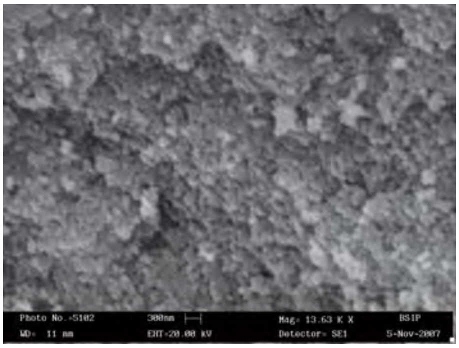
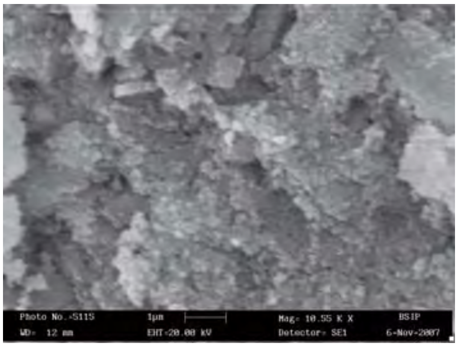
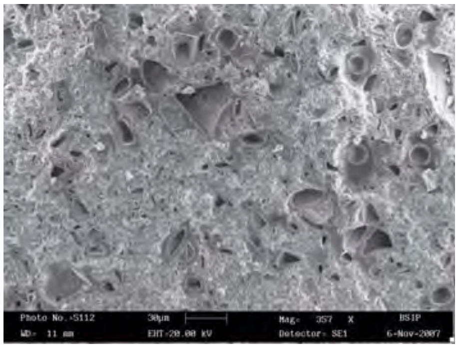
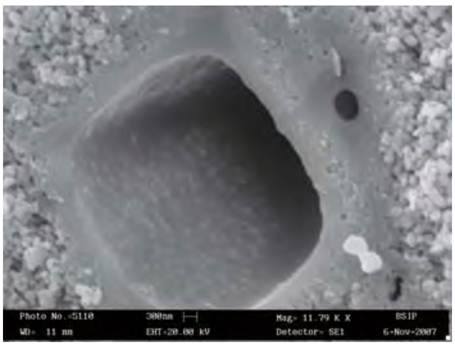


Fig. 1. Scanning electron micrograph of pellet of sensing material at room temperature.





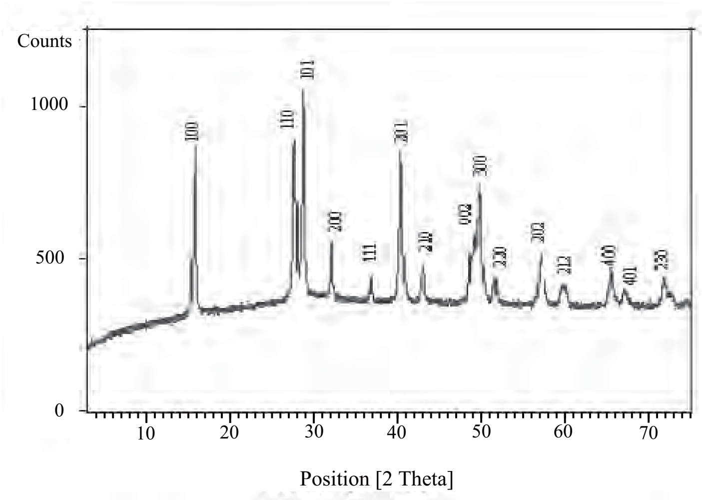
(a) (b)



(c)

Fig. 2. (a) Scanning electron micrograph of pellet of sensing material annealed at 200°C; (b) scanning electron micrograph of pellet of sensing material annealed at 400°C at microscale; (c) scanning electron micrograph of pellet of sensing material annealed at 400°C at nanoscale.

(a)



(b)

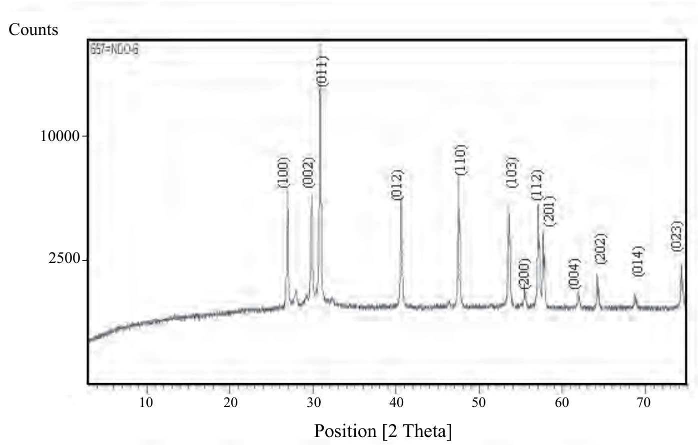


Fig. 3. (a) XRD pattern of Nd_2O_3 powder (unannealed); (b) XRD pattern of Nd_2O_3 powder annealed at 400°C.

Fig. 3(b). All the peaks correspond to Nd_2O_3 with improved crystallinity. The lattice parameters are a = 3.8310, b = 3.8310 and c = 5.9990. The crystal system is hexagonal. The average crystallite size (D) of the sensing material can be calculated by the Scherrer's formula, which is given by

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

where K = 0.94 is Scherrer's coefficient, which depends on the shape of the crystallite and the type of defects present, λ is the wavelength of X-ray radiation, β is the full width at half maximum (FWHM) of the diffraction peak and θ is the angle of diffraction. The particle size calculated from Scherrer's formula varied from 100 to 110 nm.

3.3 *Percentage mass loss*

As the sensing material is hygroscopic, its mass loss was investigated and the percentage variation of consistency in mass of the sensing material after annealing at 200, 400, 600 and 800°C for 2 h was observed. The result is shown in Fig. 4 and shows that as the annealing temperature increases, the mass of the sensing element decreases owing to the removal of water vapour.

4. Experimental Method

The experimental setup in this study consists of a controlled humidity chamber, a hygrometer, a thermometer and a digital multimeter. A saturated solution of potassium hydroxide was used as a dehumidifier and a saturated solution of potassium sulphate was used as humidifier. A pellet, which was prepared as a sensing element, was placed in a conductivity-measuring holder with a Cu electrode-pellet-Cu electrode arrangement and then was exposed to humidity inside a specially designed controlled humidity chamber. The humidifier/dehumidifier was kept in a dish over a stand. During the experiments, the temperature of the chamber remained constant. In the first step of the experiment, the chamber was dehumidified to 15% RH using the dehumidifier and then humidity in the chamber was produced using the humidifier. The accuracy of the hygrometer (Huger, Germany) used here is 1% RH and that of the thermometer is 1°C. Each sensing element was thermally annealed at temperatures of 200, 400, 600 and 800°C for 3 h in an electric furnace. After each step of annealing, the pellet was exposed to humidity. Variations in the resistance with changes in relative humidity were recorded.

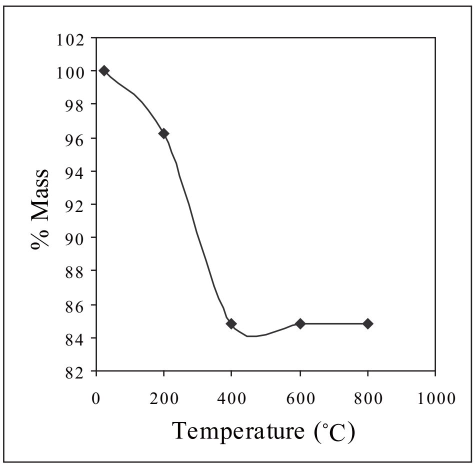


Fig. 4. Percentage of mass of sensing material vs annealing temperature.

5. Principle of Sensor Operation

A ceramic humidity sensor exhibits chemical resistance. The conductivity of a ceramic material varies with the amount of water adsorbed through its surface.[10] This principle is employed for the measurement of moisture in all resistive-type humidity sensors.

The sensitivity of a humidity sensor has been defined as the change in resistance (ΔR) of the sensing element per unit change in relative humidity (%RH),[11] i.e.,

$$S = \frac{\Delta R}{\Delta \mathrm{RH\%}} \quad (\mathrm{M\Omega/\%RH}). \tag{2}$$

The sensitivity of the sensor after annealing at different temperatures was calculated. The sensor response of a sensing material[12] is defined as

$$SR = |R_a - R|/R_a, \tag{3}$$

where R_a is the resistance of the sensing element in air and R is the resistance in a humid atmosphere.

6. Results and Discussion

Variations in the resistance with changes in %RH for the sensing element of neodymium oxide annealed at different temperatures are shown in Fig. 5. It was observed that as %RH inside the chamber increases from 15 to 95%, the resistance of the sensing element decreases.

The curve in Fig. 5 for the sensing element prepared at 25ºC has a lower gradient for the entire range of RH and has an average sensitivity of 7 MΩ/%RH. The curve for the

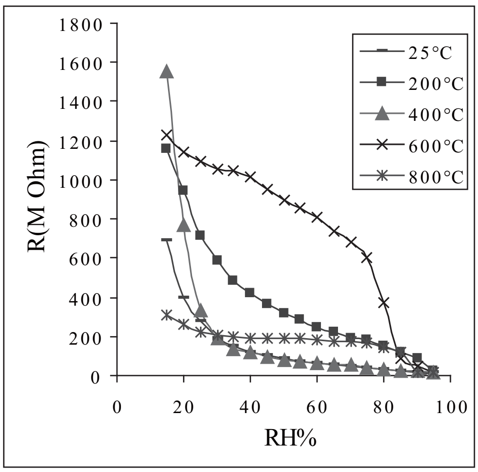


Fig. 5. Resistance vs %RH for sensing element annealed at different temperatures.

sensing element annealed at 200ºC exhibits a steady decrease in resistance with increasing %RH with higher sensitivity (14 MΩ/%RH). The curve for the sensing element annealed at 400°C exhibits an abrupt decrease in resistance from 15 to 30% RH with a maximum sensitivity of 92 MΩ/%RH and a slowly decreasing resistance at higher humidity. The average sensitivity is 19 MΩ/%RH over the entire range of RH. The curve for the sensing element annealed at 600ºC exhibits a different behaviour from the others. In the low humidity range, the change in resistance is slight, and in the higher humidity range, the resistance decreases rapidly resulting in high sensitivity. The average sensitivity is 15 MΩ/%RH. The curve for the sensing element annealed at 800ºC shows the lowest slope over the entire range of RH and the lowest average sensitivity of 4 MΩ/%RH.

The change in the impedance of porous ceramics at different humidities is related to the water adsorption mechanism on the oxide surface. The negatively charged oxygen of the water molecule is electrostatically attracted to the positively charged cationic side of the metal oxide surface. If the charge density of the cationic side is low, then water remains physically adsorbed at the surface by a weak electrostatic field. If the charge density of the cationic side is high, then water remains chemisorbed at the surface by a strong electrostatic field. The irreversible reaction at the first layer of water vapour adsorbed on metal oxide surface can be given as

$$M^+ + H_2O \rightarrow M\text{-}OH + H^+. \quad (4)$$

Fripiat *et al*. and Anderson and Parks[13–14] concluded that the weakening action of the surface electrostatic field promotes the dissociation of physisorbed water molecules in the following manner:

$$2H_2O \leftrightarrow H_3O^+ + OH^-. \quad (5)$$

The transport of charge carriers in pure water occurs by the attachment of a proton to a water molecule forming a hydronium ion. Without rotating, the hydronium ion donates another proton to a second water molecule, which accepts this proton, while a third proton becomes attached to a water molecule, and so on, throughout the liquid. This process is called a Grotthus chain reaction. The hydronium ion is most likely to be the charge carrier and responsible for the electrical conduction.

The sensitivities of the sensors prepared at different temperatures were also calculated. The sensitivity of the sensor prepared at room temperature was found to be 7 MΩ/%RH, and the sensing element annealed at 400°C exhibited the highest average sensitivity (19 MΩ/%RH) over the entire range of RH, i.e., from 15 to 95% RH. The variation of sensitivity with annealing temperatures of sensing element is shown in Fig. 6.

The reproducibility of results for sensors prepared at different temperatures was also studied. The best reproducibility was achieved at a higher range of RH for the sensing element annealed at 400°C as shown in Fig. 7. From the characteristics shown in Fig. 4, it is evident that the mass loss of the sensing material depends on the annealing temperature[15] and a maximum mass loss of 11.43% is obtained as the temperature is increased from 200 to 400ºC.

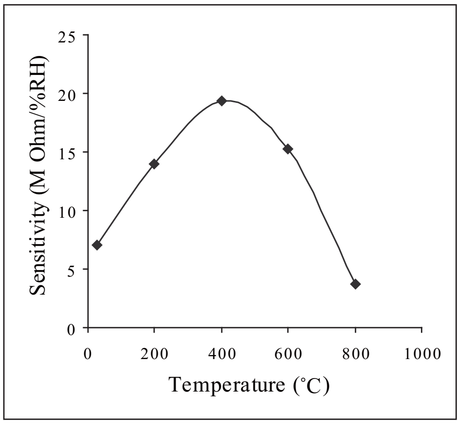


Fig. 6. Sensitivity vs annealing temperature of sensing element.

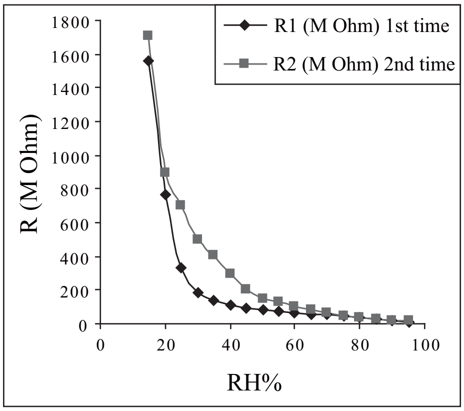


Fig. 7. Reproducibility of results for sensing element prepared at 400°C.

7. Conclusions

The sensing element annealed at a temperature of 400°C was found to have better sensitivity than those annealed at other temperatures. Its average sensitivity was 19 MΩ/%RH over a range of RH from 15 to 95%. Results were found to be reproducible and no aging effect was observed. Thus, it was found that neodymium oxide nanoparticles exhibit good sensitivity to humidity. Our investigations are in the primary stage; however, we may conclude that this material will prove to be an excellent sensor for humidity measurements for future packaging and storages applications.

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