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Improvement of Ethanol Sensing Properties of Nanocrystalline Bi_2O_3 by Doping 5.0 wt% Indium

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ABSTRACT

Present paper reports the enhancement in ethanol sensing properties of Bismuth oxide (Bi_2O_3) by doping 5.0 wt% indium (In). The nanocrystlline Bi_2O_3 were prepared by ethyl alcohol mediated decomposition route. Chemical structure of prepared pure and doped Bi_2O_3 was study bu using FT-IR. The absorption band observed at about 443.00, 509.00 and 543.00 cm−1 in FTIR spectra can be attributing to α-Bi_2O_3. Thereafter, microstructure of pure and doped Bi_2O_3 were observed by using X-ray diffraction (XRD). Further to study the conductance responses a thick films of nanocrystalline Bi_2O_3 powder were formed. The prepared films were then exposed different reducing gases. Result shows that film doped with 5.0 wt% In shows a improvement in sensing response to 50 ppm ethanol.

Keywords:—*Nanostructured; Bismuth oxide; XRD; Dopant; TEM*

I. INTRODUCTION

The introduction of new material and continuous improvements in manufacturing technologies in current technology resulted to produce a high-speed, low-power and low -cost sensor devices [1]. From last decade it is observed that lost of materials such ZnO, TiO_2, Fe_2O_3, WO_3, and SnO_2 are reported as materials for gas sensing applications.

The electrical, structural and other properties of such oxides materials can be tailored by varying material formulation, precursor raw materials, as well as various fabrications and processing conditions. Among metal oxides, bismuth trioxide has been intensively studied due to their wide band gap, high refractive index, high photoconductivity, transparency and mechanical strength immerging gas sensing application [2]. In addition to this because of particular electrical, optical and fast-ion conducting characteristics Bi_2O_3 are suitable for variety of applications including catalysts, electrical ceramics, solid-state electrolytes, gas sensors, superconductors [3-5]. Bi_2O_3 appears in four polymorphic modifications denoted as α-, β-, γ - and δ-Bi_2O_3 [6]. There are various methods has been reported to prepared Bi2O3 nanoparticles, e.g. precipitation, flame spray pyrolysis and sol–gel methods. It is well known that catalytic properties and semiconducting properties of metal oxides based sensor materials are combined together to improve the gas sensing properties. The gas sensing properties depends basically on the catalyst and surface chemical properties of sensing materials used. The gas sensing properties can be tailored often significantly by doping foreign materials to the sensing materials [7-9]. Several materials were reported for the ethanol sensor [10-11]. From literature survey it is observed that least work has been reported on Bi_2O_3 as an ethanol sensor.

The paper presents the synthesis of nanocrystalline Bi_2O_3 by thermal decomposition route in the aqueous medium of ethyl alcohol. Further the investigation of influence of 0.5% of indium doping on the structural, morphological, and electrical and ethanol gas sensing properties of Bi_2O_3 have been analyzed in details.

II. EXPERIMENTAL

2.1 Synthesis of nanocrystalline pure and doped Bi_2O_3 powders :

The mixture of bismuth nitrate $[Bi(NO_3)_3{\cdot}H_2O]$ powder and absolute ethanol was stirred for ~2 hours at 70°C temperature and then the suspension was transferred into a Teflon lined stainless steel autoclave. The temperature of the autoclave was raised slowly to 170°C and maintained for 10 h. Thereafter, the autoclave was allowed to cool naturally to room temperature and the resulting product washed several times with deionized water and absolute ethanol to remove the possible residue. Then the product was kept for drying overnight at 100°C in an oven, which was followed by calcinated at 600°C and for 6 h. Depending on the required In -doping $[In(NO_3)_3{\cdot}H_2O]$ was added separately to the mixture of bismuth nitrate and absolute ethanol. In the present study, doping concentration of indium was kept at 5.0wt%.

Further the synthesized pure and doped Bi_2O_3 were characterized using different techniques. The X-ray diffraction (XRD), (Model: Philips X'pert) with copper target, K_α radiation (λ = 1.54059 Å) was used to analyzed crystal phases Bi_2O_3. The morphologies of the synthesized powder were observed through a transmission electron microscopy (TEM), (Model: Philips CM 200). Further the chemical properties were studied by using FT-IR spectra were obtained on Magna 560 FT-IR spectrometer with a KBr disk.

III. RESULTS AND DISCUSSION

a) Material characterizations:

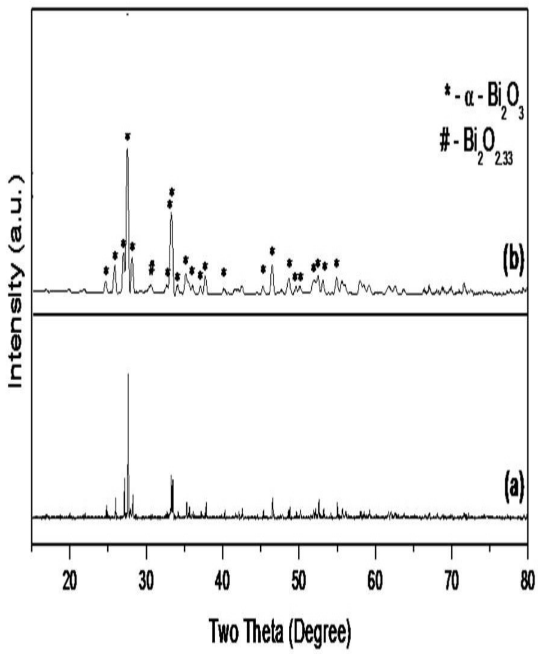

Figure 1: XRD patterns of (a) pure Bi_2O_3 and (b) 5.0 wt% In-doped Bi_2O_3 calcinated at 600°C.

Figure 1 shows the XRD pattern of pure and 5.0 wt% In-doped Bi_2O_3, calcinated at 600°C and for 6 h. From XRD pattern the formation of monoclinic α-Bi_2O_3 along with the traces of non-stiochiometric Bi_2O_3 phases in 5.0 wt% In-doped is found. The result indicates that the powder has a high degree of crystallinity as shown by the highly intense and sharp peaks. From figure all diffraction peaks are assigned to bismite crystallized in monoclinic form (α-Bi_2O_3) corresponding to JCPDS Card No. 01-072-0398. For the pure Bi_2O_3, only α- Bi_2O_3 phase was detected after cooling down to room temperature. While after doping the 5 wt% of In the there in introduction of additional phases and change in temperature range of phase stabilization.

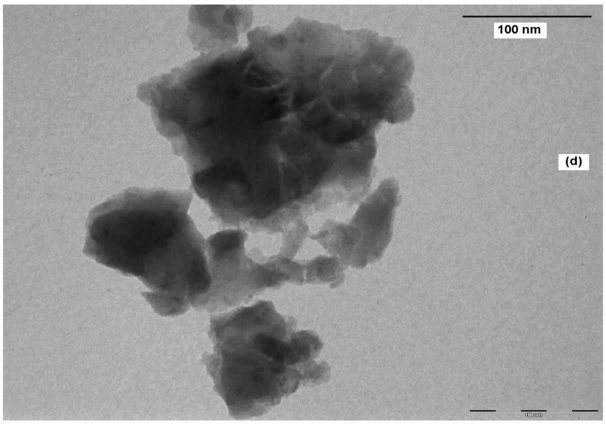

Figure 2: TEM images of 5.0 wt% In-doped Bi_2O_3 calcinated at 600 ^0C

The TEM image of the pure and doped Bi_2O_3 is depicted in Figure 2. From figure it can be seen that nanoparticles of pure and 5.0 wt% In-doped Bi_2O_3 are well dispersed without evident agglomeration.

b) Fourier transform infrared spectroscopy (FT-IR):

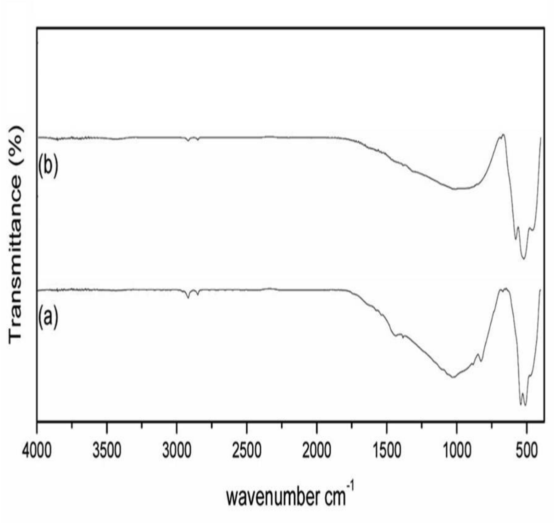

Figure 3: FTIR spectra of (a) pure Bi_2O_3, (b) 5.0 wt% In-doped Bi2O3 calcinated at 600 ^0C.

The IR spectra of pure and 5.0 wt% In-doped Bi_2O_3 samples calcinated at 600°C are depicted in Figure 3. The strong absorption band in the 544.00–443.00 cm^{-1} range. This is due to Bi–O stretching mode. The peaks around 600.00–400.00 cm^{-1} range is can be associated to stretching and deformation Bi–O modes. In the present investigations, the absorption band at about 443.00, 509.00 and 543.00 cm^{-1} in FTIR spectra can be assigned to α-Bi_2O_3 [12]. Furthermore, a shift of the bands was observed, suggesting a possible substitution of Bi^{3+} by dopand ions.

c) D.C Electrical conductivity measurements

The dc electrical conductivity of the Bi_2O_3 based thick films as a function of temperature in the range 323–623 K is investigated by using the two-probe method. Figure 4, shows the variation of the log σ with 1000/T which confirm semiconducting nature of pure Bi_2O_3 materials.

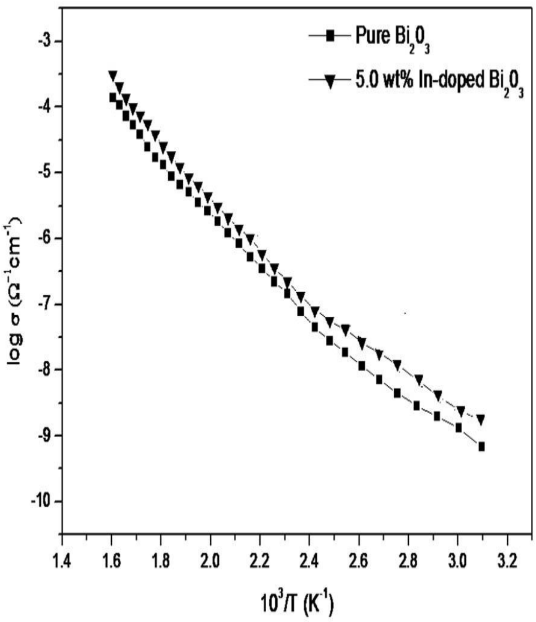

Figure 4: Variation of log (σ) versus 10^3/T for pure and In-doped bismuth oxide thick films.

Figure 4 illustrate the two conspicuous activation energy regimes; for lower temperatures and for higher temperatures. The predominance of grain boundary scattering leads to low activation energy in the lower temperature regime. Position of trap levels in the semiconductor forbidden band towards the lower limit of the conduction observed at higher temperatures, leading to increase in activation energy [13].

c) Gas sensing studies of nanocrystalline pure and 5.0 wt% In-doped Bi_2O_3

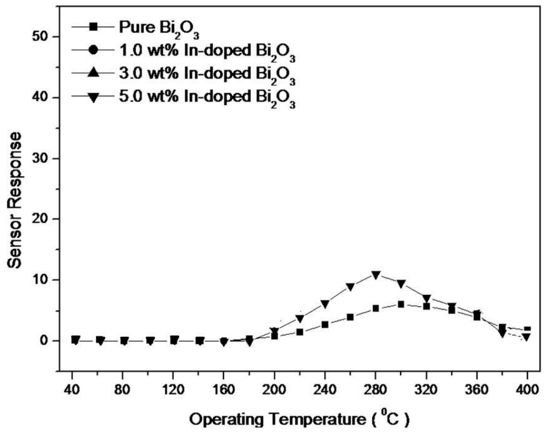

Figure 5: Sensor response of In-doped Bi_2O_3 to 50 ppm C_2H_5OH as a function of operating temperature.

Figure 5 illustrated the effect of 5.0 wt % Indium content on ethanol sensing properties of Bi_2O_3 based sensors. From the obtained results, It s found that the sensor prepared using 5.0 wt % In doped shows a enhancement in response towards ethanol vapors as compared with pure Bi_2O_3. Further, optimal operating temperature was observed to be reduced from 300°C to 280°C. The reason could be that In addition enhances the activity of the surface adsorbed oxygen and make it easy to react with ethanol. In other words In addition could enhance the oxidation of ethanol. The 2 times increase in the response of 5.0 wt% In-doped Bi_2O_3 towards ethanol may be related to the presence of non-stiochiometric $Bi_2O_{2.33}$ and basic nature of investigated dopant.

IV. CONCLUSION

Nanocrystalline pure and 5.0% In-doped Bi_2O_3 powder samples were successfully prepared by ethyl alcohol mediated decomposition route. The prepared materials showed p-type semiconducting properties. From the result the pure Bi_2O_3 based sensors showed a enhanced response to 50 ppm C_2H_5OH gas as compared with other tested reducing gases. Further it also exhibited a large response and good selectivity to ethanol, and good response-concentration linearity at 280°C. Also, optimal operating temperature was observed to be reduced from 300°C to 280°C after doping. Such enhanced performance of 5.0 wt% In-doped Bi_2O_3 to 50 ppm C_2H_5OH may be because of basic nature of In and mixed phase composition of Bi_2O_3. In conclusion such Bi_2O_3 based sensor with enhancement in sensing properties can be used as ethanol sensor.

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