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Tuning Operating Temperature of $BaSnO_3$ Gas Sensor for Reducing and Oxidizing Gases

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Abstract. Barium stannate ($BaSnO_3$) was prepared by solid state ceramic route. The crystalline phase of the prepared sample was confirmed by X-Ray Diffraction (XRD) pattern. Gas sensing behaviour of barium stannate was investigated for reducing and oxidizing gases; such as butane, ethanol, CO and NO_2; from 5 ppm to 50 ppm levels of concentration. Barium stannate sensors were optimized for highest responsiveness by varying operating temperature between 270 ^oC to 550 ^oC. Its highest response was observed for ethanol at 300^o C. The gas sensing response of ethanol was better than other gases at all the operating temperatures. Such studies in conjunction with gas sensing tests can be used for setting the optimum operating temperatures and can be used for low concentration ethanol sensing applications.

INTRODUCTION

Barium Stannate is a perovskite material generally used for dielectric and gas sensing applications [1-2]. Perovskite based resistive gas sensors work on the principle of change in the resistance, when the sensor is allowed to interact with the test gas [3]. Barium stannate has been found responsive towards gases like ethanol, LPG, NO, CH_4, CO, H_2 etc. [4-5]. Researchers have generally done sensing on this material at high operating temperatures (600-1000 ^oC) [6]. The detection of low ppm of gas concentration at lower operating temperature is in great demand for high performance, energy efficient sensing devices. In the present work, we adopted solid state ceramic route of sample preparation. The sensors were tested for the low concentrations of both reducing and oxidizing gases such as butane, ethanol, CO and NO_2 (5 - 50 ppm). Sensing at low ppm levels is imperative for several applications such as food stuff quality control, environmental monitoring and breath analysis amongst others. The operating temperature has been optimized in the range from 270 ^oC to 550 ^oC. This has been done to find out the best responsiveness of the barium stannate sensor for all the gases.

EXPERIMENTAL

Barium Stannate powder was synthesized by solid state ceramic method, mixing high purity barium carbonate (Sigma-Aldrich, purity > 99.9%) and stannic oxide (Aldrich Chemicals, purity > 99%) precursors in the required stoichiometric ratio. The mixture was ground for an hour by hand using mortar pestle followed by calcination at 1300 ^oC for 4 hrs [7].

Room temperature powder XRD was carried out using Cu-k_α radiation (1.5418 Å) on Discover D-8 X-ray diffractometer. The calcined powder was filled in a circular dye of 10 mm diameter to press under a uniaxial hydraulic pellet pressing machine. SEM images were collected from its fractured portion using a Jeol JSM- 6610 microscope.

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Calcined barium stannate powder was mixed with an organic binder (ESL-400, Reading, UK) and screen printed 3 layers onto alumina tiles using commercial screen printer DEK1202. These 3 mm × 3 mm alumina substrates coated with comb shaped gold electrodes on the top layer were used for taking resistive measurements. A platinum heater track is embedded at the back of alumina tile to set a required operating temperature. These printed tiles were annealed at 600 ^{o}C for one hour to remove organic binder and later these were bonded to their plastic housings using platinum wires (Alfa Aesar) by spot welding [8]. The Sensors were aged for two days at 500 ^{o}C and then tested for sensing purpose. An initial purge of synthetic air was given to the sensor for 1800 seconds to set its base line resistance. After this, alternate gas purges of required concentrations of test gas and synthetic air were allowed to pass for 600 and 1200 seconds, respectively [8-9]. The gas-sensitive response is defined as the ratio Ra/Rg for n-type and Rg/Ra for p-type materials in case of reducing gas, where Ra and Rg are sensors' electrical resistance measured in the air and in the test gas, respectively. The formulae are reversed for the oxidizing gases [3].

RESULT AND DISCUSSION

The XRD pattern of barium stannate sample is shown in figure 1. Barium Stannate was found crystalline and possessed cubic perovskite structure. It shows a single phase structure, which can be matched with the Joint Committee on Powder Diffraction Standards (JCPDS) card no. 15-0780 [10]. Its lattice constant determined from the peak position was calculated as 4.1124 Å, which is in close agreement with the reported value (4.116 Å).

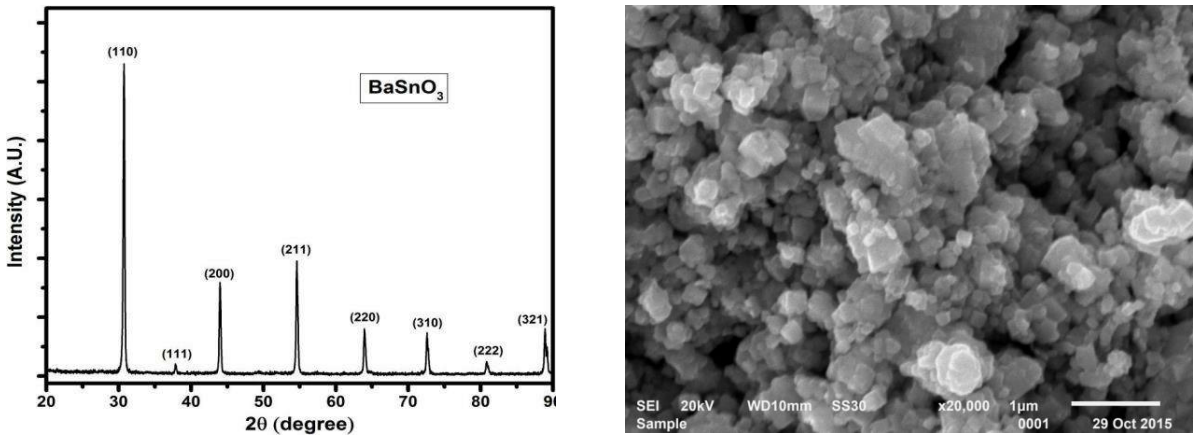

Figure 1. (a)X-Ray Diffraction pattern and **(b)** SEM micrograph of barium stannate ($BaSnO_3$)

Barium stannate exhibits a cubic structure at room temperature. Figure 1(b) shows a SEM image of barium stannate obtained from the fractured pellet portion. Cubic crystals of barium stannate can be seen in these micrographs. The average particle size calculated from imageJ software was ~ 161.46 nm with a standard deviation of 23.63 nm. Small value of standard deviation ensures a uniform grain growth and its small particle size avails more surface area which significantly gives more absorption sites for better sensing application.

Gas sensing response of barium stannate was investigated for four gases; such as butane, ethanol and CO as reducing gases and NO_2 as an oxidising gas. Figure 2(a) and 2(b) represent the gas sensing response of barium stannate at 270^{o}C and 300 ^{o}C. Butane and CO didn't respond at 270 ^{o}C but ethanol displayed a response value of 27 at this temperature for 50 ppm gas concentration. At 300 ^{o}C, the sensor showed a high response value of 85 towards ethanol and a very small response for butane was observed. The sensor showed no response to CO. For NO_2, the sensor resistance was found to be decreasing consistently but it was not saturating to any value in this temperature range for the given time. So, its responses are not included in these graphs. All the responses were found to increase with increase in the test gas concentration.

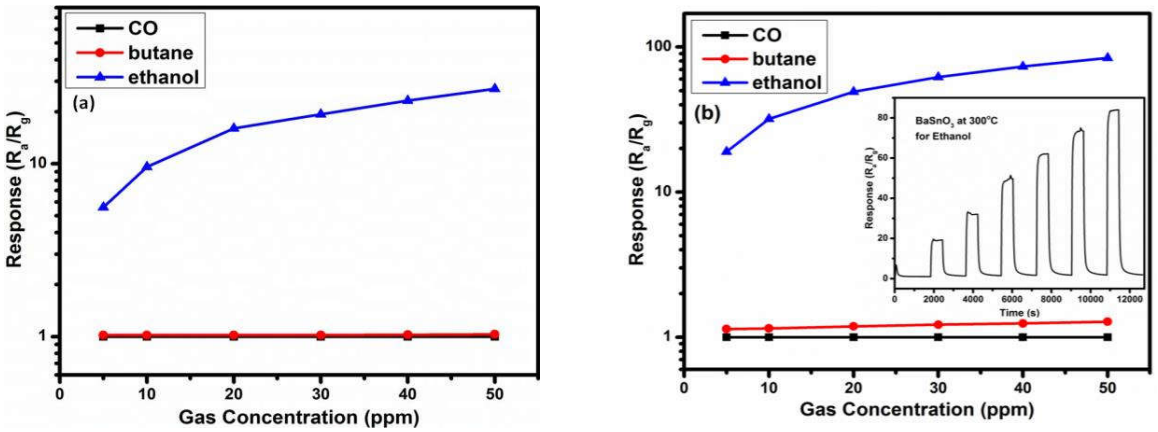

Figure 2. Gas sensing responses of barium stannate at **(a)** 270 °C and **(b)** 300 °C for CO, butane and ethanol, **2(b)** (inset) response vs. time graph of barium stannate at 300 °C for ethanol

Sensors were also tested at 400 °C and 500 °C, which are shown in figure 3(a) and 3(b). At 400 °C; CO gas showed a very small response. Ethanol responded better than the rest of the gases at all temperatures. In case of NO_2, The resistance value of sensor got saturated from this temperature. At 500 °C; the responsiveness of the sensor for CO was improved, so the sensor was further operated at 550 °C, shown in figure 4(a). It was also observed that the responses for NO_2 and butane were lowered with increase in temperature.

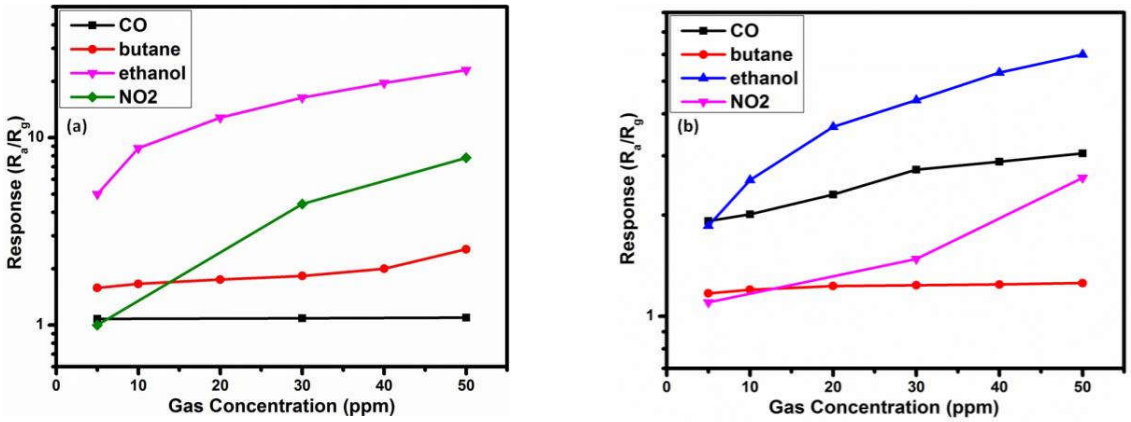

Figure 3. Gas sensing response of barium stannate at **(a)** 400 °C, **(b)** 500 °C operating temperatures

Adsorption and desorption phenomenon at the sensor surface are temperature activated. Oxygen adsorbs at the sensor surface and traps its electrons by forming oxygen anions. Change in resistivity occurs when the test gas interacts and changes the concentration of adsorbed oxygen ions. The rate at which test gas interacts with the surface adsorbed anions is also different at different operating temperatures. At a particular temperature sensors give maximum sensitivity, below this the rate of reaction is slow. At a higher temperature, the redox reaction occurs very fast, such that the test gas becomes diffusion limited and the sensor doesn't observe the change [8,11]. The response for ethanol was observed to be the maximum at 300 °C. Reducing gases oxidize (Redox reaction) at the sensor surface causing change in its resistance. The rate of redox reaction can be different at every temperature for each individual gas. Gases like ethanol get oxidize easily and give response even at low temperature. The Sensors didn't show any response for butane at low operating temperature (270 °C) but showed better responses at elevated temperatures inferred its dependence on the operating temperature. The best response of 1.6 for butane was recorded at 400 °C. Oxidation of CO into CO_2 is most likely and happens very fast at higher temperatures (>400 °C) [12]. So, barium stannate showed noticeably good response at 500 °C for CO. The responses were further reduced at 550 °C.

Oxidizing gas, NO_2 showed well saturated gas responses at and above 400 °C. Its response value at 500 °C was found lower than its responses obtained at 400 °C. The sensor response for an oxidizing gas like NO_2 is adsorption dependant. Its response reduced as the adsorption decreased with increasing temperature [13].

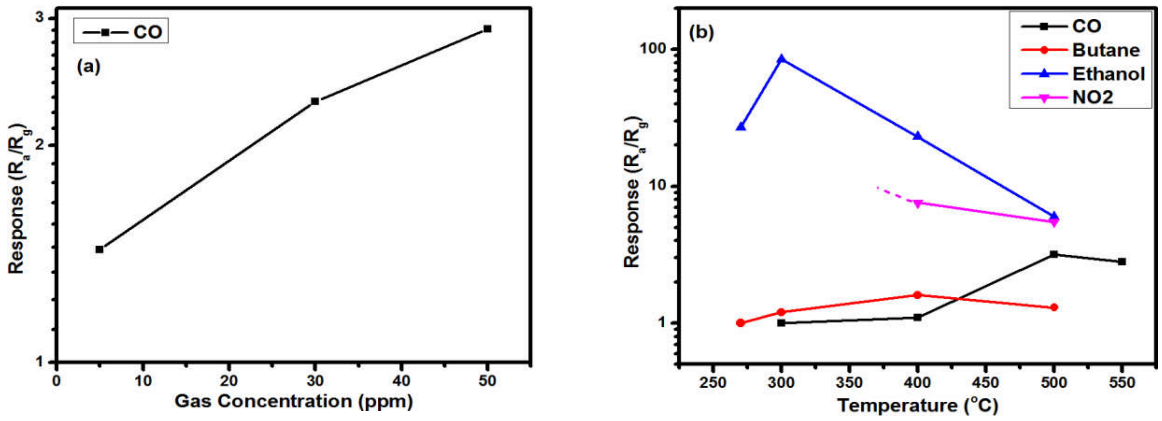

Figure 4. (a) $BaSnO_3$ sensing Response for CO at 550 °C **(b)** Sensing response for four gases with varying operating temperature

CONCLUSION

Barium stannate was prepared by solid state ceramic route. It was operated at different temperatures from 270 °C to 550 °C. The phase of prepared sample was confirmed by its XRD pattern. SEM images substantiated the formation of cubic grains of 161nm average particle size. Ethanol showed best sensing response at 300 °C while butane and CO displayed highest responses at 400 °C and 500 °C, respectively. Furthermore, NO_2 gave its first saturated response at 400 °C which was found to be decreasing on further increase in the temperature. Ethanol demonstrated the highest sensing response at all the operating temperatures.

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