Gas sensing performance of Barium Strontium Titanate thick film resistors

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Abstract. Barium Strontium Titanate (BST-(Ba0.87Sr0.13)TiO3) ceramic powder was prepared by mechanochemical process. The thick films of different thicknesses of BST were prepared by screen-printing technique and gas-sensing performance of these films was tested for various gases. The films showed highest response and selectivity to ammonia gas. The effect of film thickness on gas response was also studied. The gas response, selectivity, response and recovery time of the sensor were measured and presented.

Keywords. (Ba0.87Sr0.13)TiO3 thick films, ammonia gas sensor, gas response, selectivity.

1. Introduction

The pervoskite oxides (ABO3) were used as gas sensor materials for their stability in thermal and chemical atmospheres. So, over a last decade, the pervoskite oxide ceramic such as BaTiO3 [1-4] and (Ba,Sr)TiO3 [5-9] have created and promoted interest in chemical sensors. Modifications in microstructure, processing parameters and also concentration of acceptor/donor dopant can vary the temperature coefficient of the resistance and conductivity of ABO3 oxides. Sensors based on ABO3–type complex oxide material, of rare earth elements have an outstanding merit of its high sensitive and selective characteristics. These characteristics can be controlled by selecting suitable A and B atoms or chemically doping A’ and B’ elements equivalent respectively to A and B into ABO3 to obtain AxA’1−xBxB’1−yO3 compound [10,11].

It is reported (9) that the response to NH3 gas goes on increasing with film thickness. It was observed in present investigation that gas response increases with increase in film thickness up to certain limit, beyond that response decreases on further increase in thickness.

2. Experiment

2.1. Powder and paste preparation

The AR grade powders, of Ba(OH)2 8H2O, Sr(OH)2 with 7:1 molar concentration and TiO2 were milled for 2h using planetary ball mill to obtain fine-grained powder. The powder was then calcined at 1000 °C for 6h. The XRD spectrum of as prepared powder confirmed the sub microcrystalline
pervoskite phase. The as prepared powder was screen printed [12,13] on glass substrate in the desired pattern.

The films of various thicknesses were prepared by controlling the number of impressions of squeeze strokes. Different films of thicknesses: 1BST(17µm), 2BST(33µm), 3BST(48µm), 4BST(63µm) were printed.

3. Results

3.1. Structural Properties

Figure 1 shows the X-ray diffractogram of screen-printed BST thick film fired at 550 °C in air atmosphere.

![X-ray diffractogram of BST thick films](image)

**Figure 1.** X-ray diffractogram of the BST thick films.

It reveals from XRD that the material is the polycrystalline in nature with tetragonal pervoskite phases. The peaks from XRD pattern are matching well with the ASTM data book, card No. 34-11. The average grain size was determined using Scherrer formula and is estimated to be 264 nm.

3.2. Microstructural analysis

![SEM images](image)

**Figure 2.** SEM images: (a) Unmodified 2BST(33µm) (b) Unmodified 4BST(63µm).
Figure 2(a) depicts the SEM image of unmodified 2BST(33µm) thick film fired at 550°C. The film consists of large number of grains leading to high porosity and large effective surface area available for the adsorption of oxygen species. Figure 2(b) is the SEM image of the unmodified 4BST film having larger thickness (63µm). It is clear from figure that it is comparatively less porous and grains are agglomerated. Effective surface to volume ratio was observed to be decreased and less number of oxygen ions would be adsorbed as compared to the film in Fig. 2(a).

3.3. Gas response with operating temperature

It is clear from the Figure 3 that the film with thickness of 33 µm was observed to be most sensitive to NH₃ gas at 300°C. This may be due to increase in porosity with thickness. As porosity increases, the in-pore adsorption of oxygen increases, leading to improve the adsorption-desorption mechanism of target gas and vice versa.

3.4. Selectivity of pure and modified film

Figure 4 shows the histogram showing selectivities of 2BST film. It is clear from histogram that
unmodified BST is more selective to NH₃.

3. 5. Response and recovery at different gas concentration

![Graph showing response and recovery profile of film to NH₃ gas](image)

Figure 5. NH₃ gas response and recovery of film at different gas concentrations

Figure 5 shows the response and recovery profile of the most sensitive unmodified (2BST) film to ammonia gas at 300 °C. Figure that the response and recovery time increases as gas concentration increases. It revealed that for lower gas concentration response and recovery times were observed to be shorter and longer as gas concentration increases.

4. Discussion

The sensitivity of (Ba₀.₈₇Sr₀.₁₃)TiO₃ to NH₃ could be attributed to the high oxygen deficiency and defect density, which would have led larger amount of oxygen adsorption. Larger the amount of oxygen adsorbed on the surface, larger would be the oxidizing capability and faster would be the oxidation of NH₃ gas. Hydride (NH₃) may have lower sensitivity than hydrogen exposed on particular metal oxide under same condition [14]. The lower response to NH₃ may be related to firm binding state preventing fast decomposition and water formation. NH₃ undergoes following reaction on exposure to metal surface:

\[
2\text{NH}_3 + O_{\text{ads}} + O_2 \rightarrow 2\text{NO}_2 + 3\text{H}_2\text{O} + 5e^- \quad \text{…………………(1)}
\]

NH₃ molecule has a lone pair of electrons. In comparison with other gases, NH₃ can readily donate the unpaired electrons to the metal ions (of base material) which has unfilled orbits to form coordination complex. Furthermore, the coordinated NH₃ molecules easily react with oxygen adsorbates (O⁻_ads) and the electrons bonded with adsorbed oxygen are returned back into the sensor, increasing the sensor conductivity.

5. Conclusion

1) The unmodified 2BST film is selective to NH₃ sensor at 350°C.
2) Gas response to NH₃ increases with increase in film thickness attains maximum for 33 µm.

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