

Gas Sensing Potential of Strontia Doped Yttria Stabilized Zirconia

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Abstract— Different samples of strontia doped yttria stabilized zirconia were synthesized by decomposition of mechanical mixture of oxalate precursors. Strontia was doped in 5 and 8 mol percent keeping yttria constant at 5 mole percent and remaining zirconia in the stoichiometry. Thermal decomposition was studied using TG and DTA from ambient to 1300°C. In another experiment, oxalate mixtures under study were heated from ambient temperature to 1300°C at the rate of 10°C/min. The detailed study on phase formation temperature were carried out by heating samples from 1000 to 1300°C and cooling the products to room temperature and recording X-ray Diffraction pattern for the in process sample. Surface morphology was studied by scanning electron microscopy. The product formed was pressed into round discs and checked for its potential for sensing various gases like NO, H₂S and acetone and responses were monitored at room temperature. The concentrations of the test gases used were in the range of 5-25 ppm.

Keyword- YSZ; strontia doped; phase formation; gas sensing

I. INTRODUCTION

Yttria stabilized zirconia (YSZ) is a widely studied ceramic compound. A lot of research work has been reported on stabilization of zirconia in partially stabilized and completely stabilized tetragonal and cubic structure. Zirconia exhibits three polymorphic forms viz. monoclinic, tetragonal and cubic. The monoclinic form of zirconia is stable at room temperature and changes to a denser tetragonal form at 1000°C [1]. There are disadvantages of using zirconia in monoclinic structure since it involves a volume change of about 4-5% during its conversion to tetragonal form resulting in to cracks in the structure [2]. Hence stabilization of zirconia is necessary in cubic or tetragonal form. Different cations have been used for stabilization of zirconia. This stabilization of zirconia makes it possible to be used in a wide range of applications. Amongst a variety of cations tried yttria in 8 to 15 mole percent, appears to be most advantageous and is a commercially available product for a wide range of applications [3].

Yttria stabilized zirconia also find varied applications in fields like thermal barrier coatings [4], dental ceramics [5], solid oxide fuel cells and gas sensors [6]. YSZ can be synthesized by co-precipitation, sol-gel, solid state and hydrothermal routes. YSZ has been prepared using different precursors mainly oxalate, hydroxide and citrate [7-10]. There are very few reports on partial substitution of strontium +2 ions in YSZ [11].

In present paper, synthesis of strontia doped yttria stabilized zirconia was carried out by mechanical mixing of oxalate salts. Characterisation of the resultant products was done by thermo-gravimetric analysis (TGA), differential thermal analysis (DTA), X-ray diffraction (XRD) and Scanning electron microscopy (SEM). The present paper reports the gas sensing potential of the final products with nominal composition ($Zr_{0.90}Y_{0.05}Sr_{0.05}O_{1.925}$ ZYS-5 and ($Zr_{0.87}Y_{0.05}Sr_{0.08}O_{1.895}$ ZYS-8. Thermal profiling of the end products from 1000 to 1300°C was carried out to determine the phase formation temperature.

II. EXPERIMENTAL

A. Materials

Raw materials used: Zirconyl oxychloride octahydrate (99.9%), yttrium nitrate tetrahydrate, strontium nitrate anhydrous, potassium oxalate monohydrate. All the raw materials used were of Fisher Scientific make and were 99.9% pure.

B. Method

Strontia doped yttria stabilized zirconia was synthesized in two different mole proportions viz. 5 and 8 by decomposition of mechanical mixture of oxalate precursors. Zirconium oxalate, yttrium oxalate and strontium oxalate were synthesized separately and then added in required stoichiometry. Zirconium oxalate was synthesized by adding zirconyl oxochloride octahydrate solution drop wise into bath of potassium oxalate monohydrate. The solution was churned for two hours, filtered, washed and dried. In similar manner, yttrium oxalate and strontium oxalate were synthesized using yttrium nitrate tetrahydrate and strontium nitrate anhydrous respectively. The oxalate salts of zirconium, yttrium and strontium were mixed in required stoichiometry and were ball milled for two hours. The oxalate mixtures were heated in alumina boats from room temperature to 1100°C. The compositions $(Zr_{0.90}Y_{0.05}Sr_{0.05})O_{1.925}$ and $(Zr_{0.87}Y_{0.05}Sr_{0.08})O_{1.895}$ will now be abbreviated as ZYS-5 and ZYS-8 respectively.

The raw, ball milled mixture was subjected to simultaneous TG/DTA from ambient to 1300°C. The ball milled mixtures of ZYS-5 and ZYS-8 were then calcined at 1000°C, 1100°C, 1200°C and 1300°C for two hours each in a temperature programmed furnace. The samples were cooled to room temperature and then subjected to X-ray Diffractometry (XRD) and scanning electron microscopy (SEM) to study the phase formation temperature and surface morphology respectively.

C. Instrumentation

Thermal analyses of the samples were carried out in an in house fabricated TG instrument. The powder samples were tested by X-ray diffractometer (Model: Bruker D8 Advance) for the crystal structure and morphology was studied by Scanning Electron Microscope (Model: JEOL JSM 6360A) for surface morphology. The gas sensing was carried out in a fabricated glass assembly using Keithley 6½-Digit Dual Display Digital Multimeter Model 2000. The pelletized samples were placed in the fabricated assembly and was exposed to different gases namely hydrogen sulphide (H_2S), nitric oxide (NO) and acetone vapours with the help of a syringe (Hamilton syringes). Change in resistance was measured using digital multimeter. The gases H_2S and NO were procured from Alchemie Gases Pvt Ltd, Mumbai and had 99.5% purity. Acetone used for sensing was procured from Fisher Scientific (AR grade).

III. RESULTS AND DISCUSSION

A. Thermal Analysis

The exothermic oxalate decomposition is expected to catalyze the decomposition of individual oxalates and hence the ternary metal oxide with composition $(Zr_{0.90}Y_{0.05}Sr_{0.05})O_{1.925}$ forms at temperature around 1100-1200°C. In our earlier work on binary and ternary oxalate mixtures [12],[13], similar type of effect has reduced the phase formation temperature by more than 250°C. Such reduced decomposition temperature presents advantage that in just decomposed state the cations formed are more active, hence single phase product formation occurs. Also, contamination or secondary binary phase formation is reduced. The product formed will be more homogeneous and uniform in particle size. Table 1 shows the details of weight loss occurred in different steps and the species lost in each step.

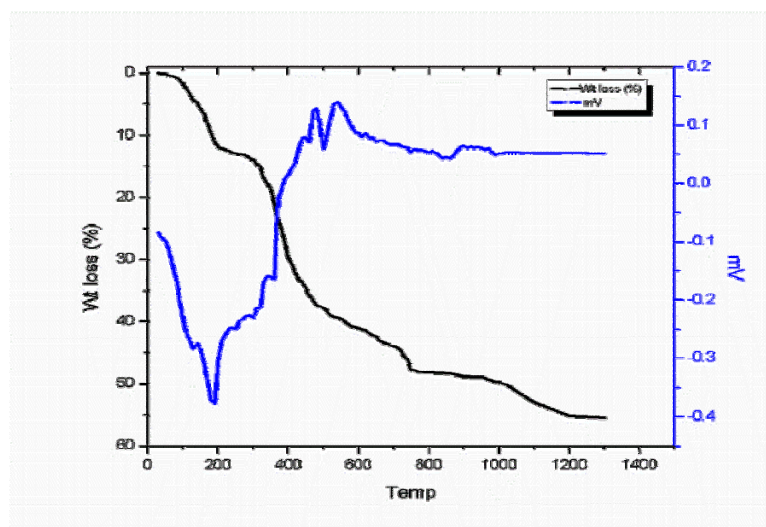


Fig. 1. TG/DTA plot of ZYS-5

Table I. TG Analysis of ZYS-5

Steps	Temperature (°C) range	% weight loss	Species lost
1	RT to 100		Adsorbed moisture
2	101 to 230	11.71	2 H ₂ O
3	231 to 950	37.28	1 CO, 2 CO ₂
4	951 to 1300	55.47	1 CO

Thermal decomposition of ZYS-8 is shown below in fig. 2

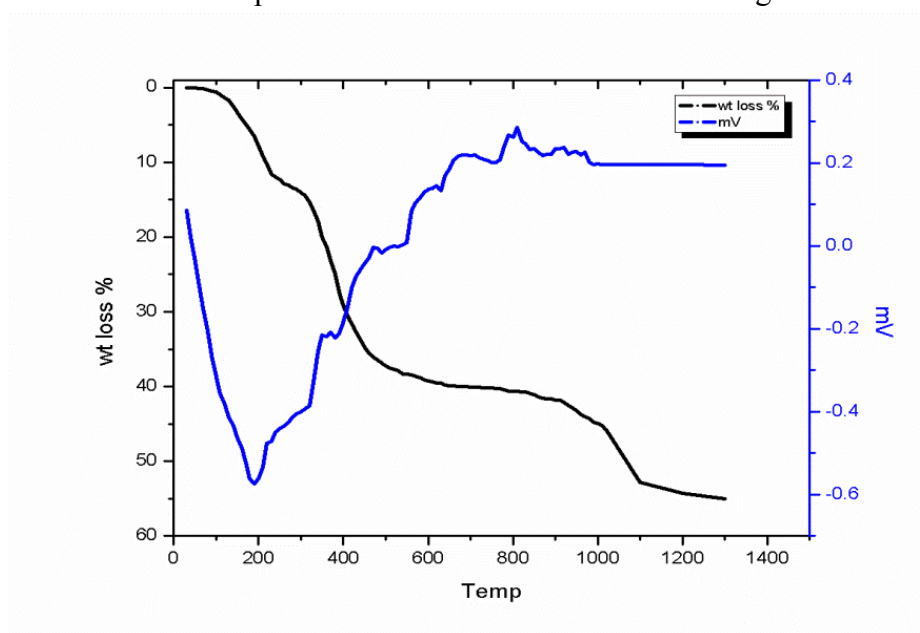


Fig. 2. TG/DTA plot of ZYS-8

The decomposition sequence with stepwise weight loss and species lost is summarised below

Table II. TG Analysis of ZYS-8

Steps	Temperature (°C) range	% weight loss	Species lost
1	RT to 110		Adsorbed moisture
2	111 to 230	10.63	1.75 H ₂ O
3	231 to 890	31.31	2 CO + 0.75 CO ₂
4	891 to 1300	55.02	0.8 CO ₂

B. XRD study

ZYS-5 heated from 1000-1300°C at an interval of 100 C is shown below in Fig. 3a

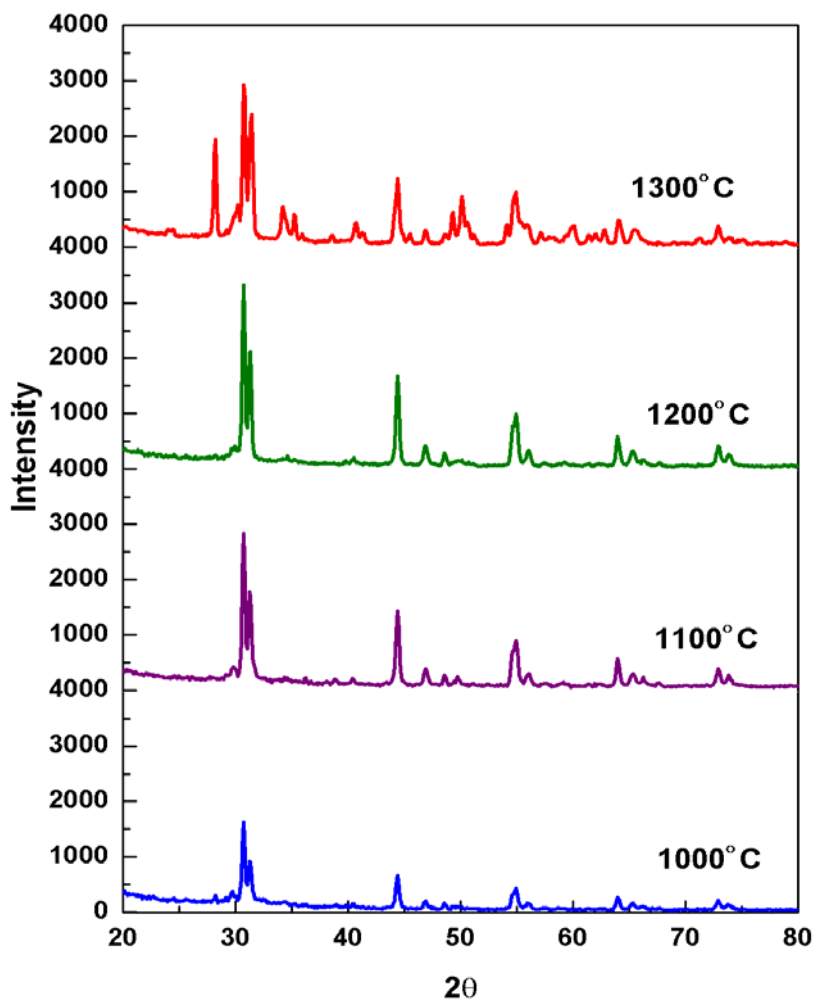


Fig.3a. XRD of ZYS-5 calcined at different temperature

From the diffraction pattern of ZYS-5 (Fig.3a), it can be observed that the phase starts forming at around 1100°C and is complete at 1200°C. Above this temperature the disintegration of the phase begins, which can be seen from the XRD pattern at 1300°C. The 100% peak starts disintegrating at around 1300°C. Major peaks are observed at 30.7°, 44.4° and 54.9° which are characteristic of cubic perovskite structure.

Fig 3b, shows XRD patterns recorded for ZYS-8 heated at 1000, 1100, 1200 and 1300°C.

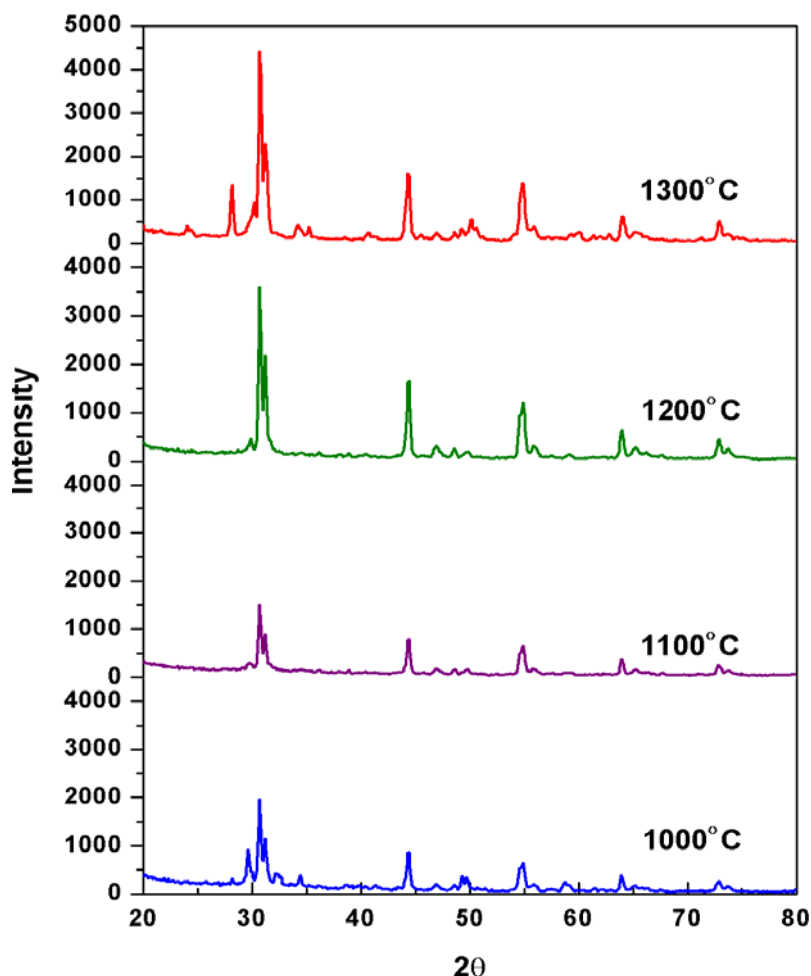


Fig.3b. XRD of ZYS-8 calcined at different temperatures

Similar is the case with ZYS-8 (Fig.3b) in which phase is seen to be disintegrated at 1300°C. On calcination at 1000°C, the crystallinity is poor. A sample heated upto 1100 shows improved crystallinity. Whereas, after heating till 1200°C, the crystal structure is well grown and the peaks are distinct. After heating till 1300°C, there is splitting of peak observed at 2 theta 30.7 and a small peak is seen at 28 which was absent at lower temperatures. The peaks are broadened and the phase seems to be disintegrated. In all above XRD patterns the 100% peak appears at 30.7° confirming formation of cubic perovskite phase.

The average crystallite sizes of both the samples calcined at different temperatures from 1000°C to 1300°C were calculated (Table III). From the values it was observed that the average crystallite size in ZYS-5 as well as ZYS-8 is highest after calcination at 1200°C. After heating at 1300°C, it was observed that the particle size decreased. Hence it can be concluded that the calcination temperature should be 1200°C.

Table III. Average Crystallite Sizes of ZYS-5 and ZYS-8

Samples	Average crystallite sizes at different temperatures			
	1000 °C	1100°C	1200°C	1300°C
ZYS-5	19.84	20.03	20.66	18.66
ZYS-8	21.41	21.55	23.83	23.54

C. SEM study

Sintered pellets of ZYS-5 and ZYS-8 heated at 1000, 1100, 1200 and 1300°C was used for SEM studies. The images obtained are shown below in Fig 4a and b.

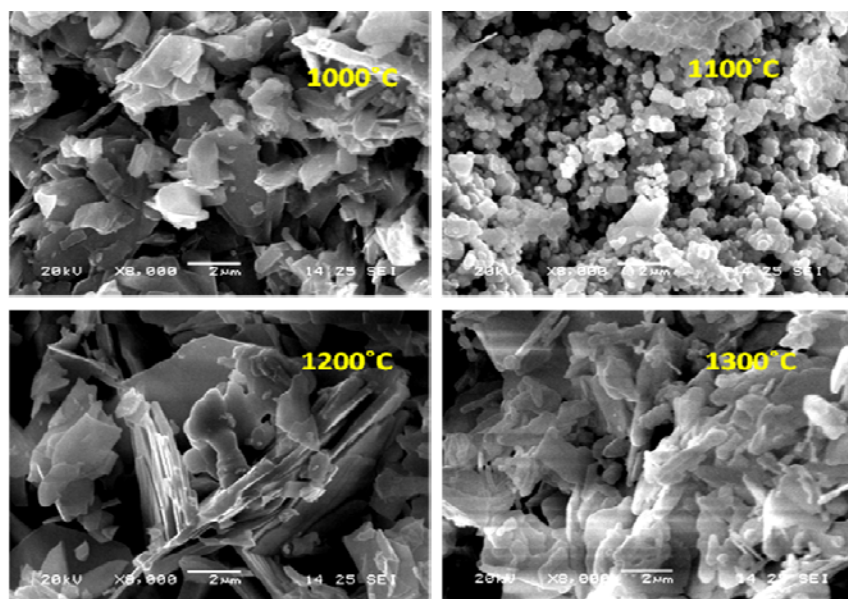


Fig. 4a. SEM micrographs of ZYS-5 calcined at different temperatures

In ZYS-5 (Fig.4a), sample heated at 1200°C shows highest particle size, more regularity, more translucence and more glassy structure amongst all temperature from 1000-1300°C. At 1100°C, the structure appears to be in transition from 1000-1100°C and 1100 to 1200°C. Therefore, for calcination and sintering, ideal temperature should be 1200°C. The structure transforms from fine laminar flakes to nano particles to fused laminar sheets and at 1300°C on top of the sheets there are depositions of smaller particles.

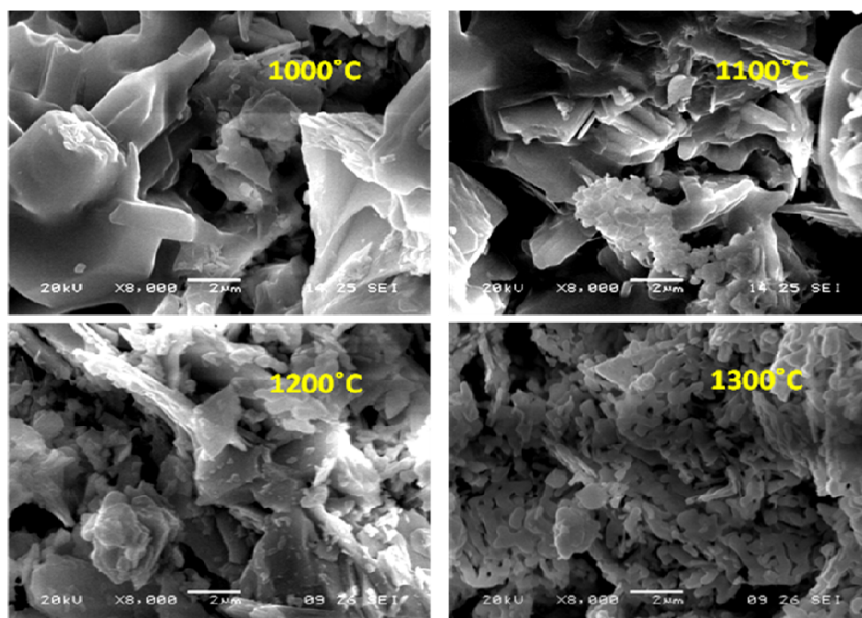


Fig.4b. SEM micrographs of ZYS-8 calcined at different temperatures

For ZYS-8 (Fig. 4 b), at 1000°C the glassy, laminar particles are formed which on further heating disintegrate into broken, smaller particles with reduction in density. Hence for ZYS-8, heating should not go beyond 1100 to 1150°C. Samples heated at 1200°C or 1300°C show charging effect as well and particle size decreases from 5 microns to a fraction of micron.

The average particle size appears to be maximum in ZYS-8 composition. With the increase in strontium percentage, there is destruction of the phase. Hence, uniformity in particle size, laminar structure and glass appearance reduces from 5 to 8 mol% of Sr.

D. Sensing study

The pellets with nominal composition $(Zr_{0.90}Y_{0.05}Sr_{0.05})O_{1.925}$ and $(Zr_{0.87}Y_{0.05}Sr_{0.08})O_{1.895}$ were used for measurement of gas sensing ability. The pellets were kept in an in-house fabricated glass assembly and were further connected to digital multimeter.

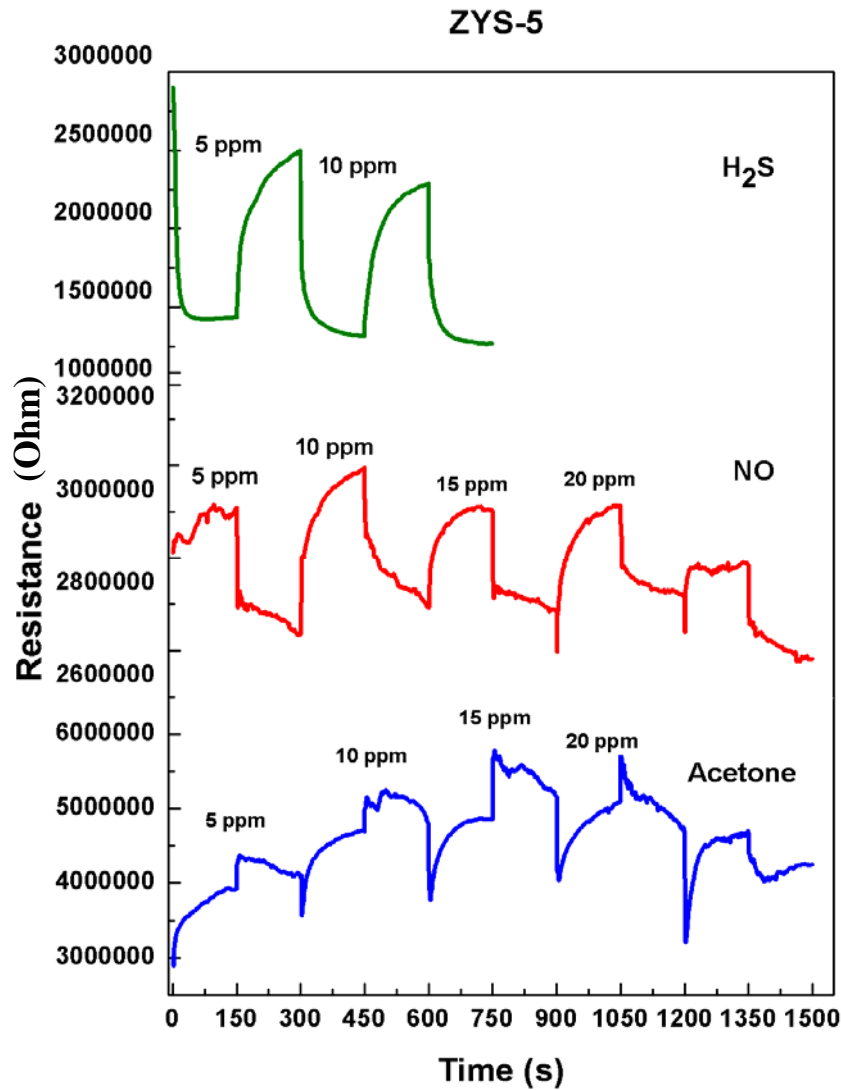


Fig. 5a. Sensing graphs of ZYS-5

It appears that ZYS-5 (Fig. 5a) shows higher sensitivity towards reducing gases like H₂S and NO. Saturation level for NO is around 20 ppm and shows excellent sensitivity in the range of 5 to 20 ppm. It is highly reproducible and at room temperature, desorption time is as low as 50 sec. ZYS-5 shows sensitivity for H₂S at around 10 ppm. The saturation level for H₂S is around 15 ppm. In case of acetone, the result is not reproducible beyond 10 ppm.

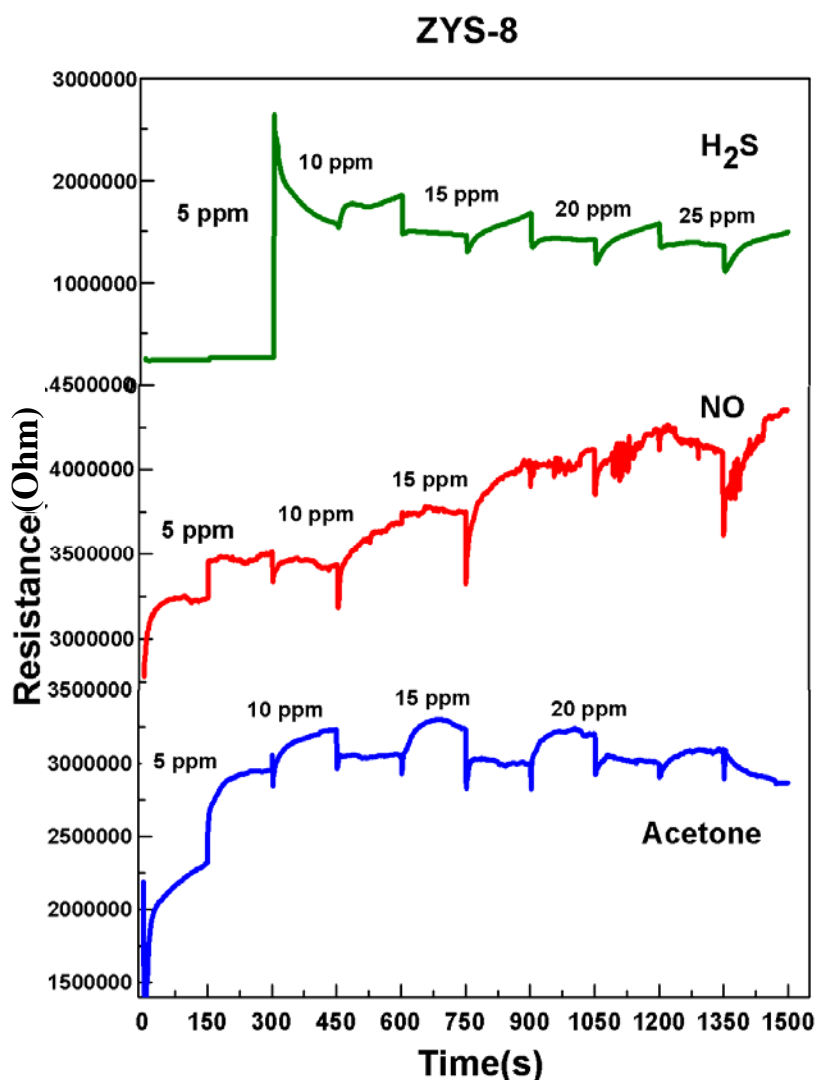


Fig. 5b: Sensing graphs of ZYS-8

ZYS-8 (Fig.5b) shows poor sensitivity towards NO and acetone but shows better sensitivity even at lower concentrations of H₂S. Both ZYS-5 and ZYS-8 can be used as in-line process equipment if there is in-situ generation of H₂S during manufacturing operations.

IV. CONCLUSIONS AND FUTURE SCOPE

- Oxalate mechanical mixtures are good precursors for synthesis of ZYS-5 & ZYS-8.
- The crystal structure is Cubic perovskit
- During oxalate decomposition dehydration, loss of CO and loss of CO₂ is observed in the temperature range 100-230, 230-950 and 950-1150⁰C respectively.
- Composition of the decomposition product are $Zr_{0.90}Y_{0.05}Sr_{0.05}O_{1.925}$ and $(Zr_{0.87}Y_{0.05}Sr_{0.08})O_{1.895}$.
- ZYS-5 shows better sensitivity towards reducing gases like NO and H₂S and no sensitivity towards acetone as compared to ZYS-8

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