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Research Paper

Comparative Study of Yttria Stabilized Zirconia Prepared by Co-precipitation Method using Various Precursors and its Potential as Gas Sensor

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Abstract: *Yttria stabilized zirconia (YSZ) have different chemical properties. These include excellent chemical resistance, refractory character, oxygen ionic conductivity and polymorphism. Due to these properties, YSZ finds many structural and electronic applications such as gas sensors, electrolyte and anode in SOFC's, dental implants and thermal barrier coatings. These interesting properties and resultant applications primarily require stabilized zirconia in tetragonal and cubic crystal structure. In present paper, synthesis of stabilized zirconia using 8 mol percent yttria was carried out by co-precipitation method. Various precursors like hydroxide, oxalate and citrate were used for the same. The phase formation was studied using X-ray Diffractometry and the surface morphology by scanning electron microscopy. The pellets were used for sensing gases like oxygen, nitrogen, hydrocarbons and NO_x etc. The response obtained for all the pellets is discussed at length. It is observed that, YSZ obtained from oxalate precursor gives better response.*

Keywords: 8YSZ, oxalate, hydroxide, citrate, precursors, YZOX, YZOH, YZCT,sensing application.

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Introduction

Zirconia is an important refractory material which is widely used in high temperature applications. Zirconia shows three polymorphic forms viz; monoclinic, tetragonal and cubic, which are stable at different temperature ranges [1]. Monoclinic form is stable at room temperature and changes to a denser tetragonal form at around 950^0C and finally transforms to cubic form at 2200^0C.Thisconversion of monoclinic to tetragonal form which occurs at about 950° C involves a volume change of about 3-5 % resulting in to cracks within the structure. During heating process, zirconia undergoes the above phase transformation. This change in volume associated with the transformation makes the usage of pure zirconia impossible.

This problem is resolved by addition of some oxides of metals like Calcium, Magnesium and Yttrium, into the zirconia in a certain degree (about 1 to 18 mol %). This results in a solid solution, which stabilizes in cubic form and has no phase transformation during heating and cooling. This solid solution is termed as stabilized zirconia, a valuable refractory. *Completely stabilized zirconia crystallizes in cubic structure and finds many applications in SOFC, thermal barrier coatings and dental ceramics. Whereas, tetragonal form of zirconia is known as partially stabilized form which is used in gas sensors, grinding media, wear resistant components, and electrochemical oxygen pump [2].*

Aim of the present work is to stabilize zirconia intetragonal form and to check its potential as a gas sensor.

YSZ can be prepared by solid state route[3]as well as wet chemical route[4] i.e.sol-gel[5], co-precipitation[2,6,7] and hydrothermalmethod [8,9].

In the present paper, 8-YSZ was prepared by wet chemical route, precisely by co-precipitation method, using various precursors: oxalate, hydroxide and citrate.

Material and Methods

8 mol% Yttria stabilized zirconia was prepared by using wet chemical method (co-precipitation method) by using three different precursors namely oxalate, hydroxide and citrate. The raw materials used were Zirconyloxychlorideoctahydrate ($ZrOCl_2.8H_2O$), Yttrium chloride (prepared by dissolving 99.99% Y_2O_3 in hydrochloric acid), potassium oxalate ($K_2C_2O_4.H_2O$), sodium hydroxide (NaOH), citric acid monohydrate

($C_6H_8O_7.H_2O$), C-TAB buffer. (All chemicals used were of AR grade and minimum purity was 99.9% obtained from LobaChemie and were used in as obtained form).

Aqueous solution of $ZrOCl_2.8H_2O$ and YCl_3 was prepared by adding desired quantity of Zr and Y salts to give final stoichiometry as 92 mol percent zirconia and 8 mol percent yttria. This solution was added drop wise with constant stirring to potassium oxalate solution which yielded white precipitate at pH 6.5 to 7. The mixture was churned for two hours and then digested for two more hours in hot water bath. This precipitate was then filtered and washed till the filtrate gave negative test with silver nitrate. The oven dried precipitate (110^0C for 2 hrs) was then calcined in a programmed furnace at the heating rate of 10^0C/min till the final temperature of 950^0C and then soaked for two hours. The calcined sample was compacted using hydraulic pellet press at 5tons pressure maintained for 30 min in a steel die of 10mm diameter. The pellets were then sintered at 1250^0C for three hours. The sintered pellet was abbreviated as YZOX.

Similar method was carried out for preparing 8-YSZ by hydroxide co-precipitation (abbreviated as YZOH) by using NaOH which resulted in formation of white gel like precipitate at pH around 13-14.

For preparing 8-YSZ by citrate co-precipitation (abbreviated as YZCT) by using citric acid monohydrate, pH of the solution was found to be around 3-4 and showed no sign of any precipitate. Hence C-TAB buffer was made alkaline and added to the solution which resulted in formation of transparent gel. As filtration of gel was not possible, purification was achieved by washing with distilled water several times followed by decantation. This gel was then oven dried at 110^0C for 2 hours which produced black powder. The black powder was calcined at 950^0C which produced white, granular powder. It was then subjected to XRD study followed by SEM.

The powder samples were tested by X-ray diffractometer (Model: BrukerD8 Advance) for the crystal structure and the sintered pellets were tested by SEM (Model: JEOL JSM 6360A) for surface morphology.The gas sensing was carried out in a fabricated assembly using Keithley 5½-Digit Dual Display Digital Multimeter Model 2110.

Results and Discussion

For YSZ, prominent crystal structures are monoclinic (undesirable), tetragonal (partially stabilized), cubic (completely stabilized). Out of these for monoclinic structure 100% peak is observed at 2θ around 28^0, for tetragonal structure 100% peak is observed at 2θ = $30.17^0$and for cubic structure 100% peak is observed at 2θ =30.11^0. In the present work we are looking for 100% diffraction peak at tetragonal or cubic.

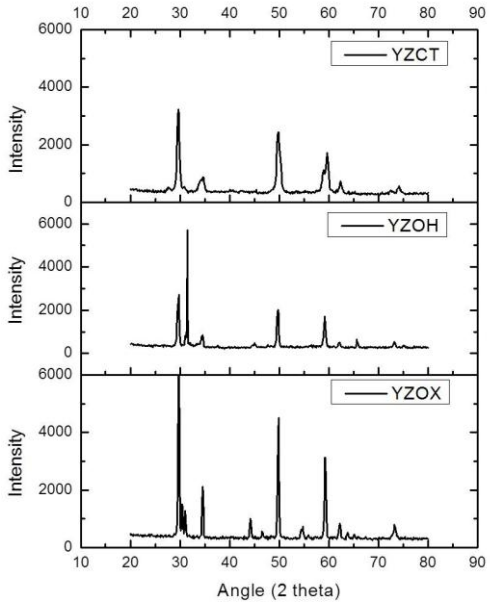

Figure 1: XRD Analysis

XRD study shows that YZOX matches with the desired tetragonal structure as reported in JCPDS pattern number 48-0224. It shows characteristic peaks at 30.1, 34.6, 50.1 and 59.4^0. YZOH shows the formation of monoclinic phase along with tetragonal phase in the structure. YZCT gave a mixture of tetragonal and cubic phases with no trace of monoclinic structure. It appears that oxalate precursor yields tetragonal phase prominently. Citrate precursor gives a mixture of tetragonal and cubic phases and hydroxide precursor is the only precursor which yields a mixture of monoclinic and tetragonal phases. Hence it appears that oxalate and citrate are better precursors as compared to hydroxide.

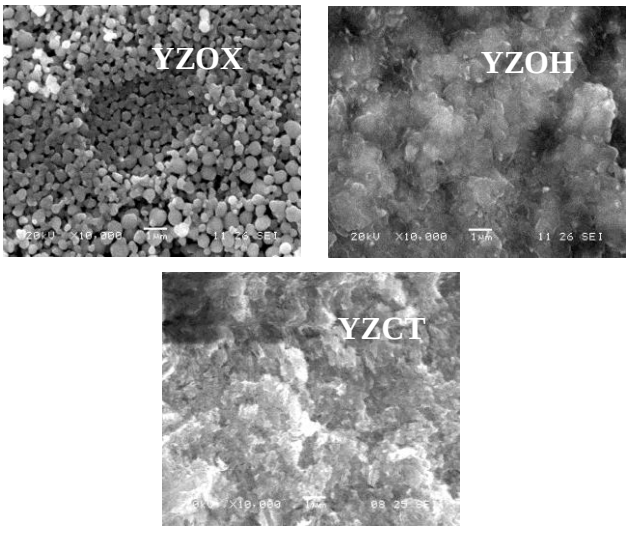

Figure 2: SEM micrographs

From SEM, it can be seen that YZOX has granular structure with high porosity and the grains are fused at edges. This feature facilitates the use of YSZ in sensors. The micrographs of YZOH and YZCT depict the fusion of grains in the structure. Due to low or no porosity YZOH and YZCT may show less or no sensitivity for gases.

The sintered pellets with nominal composition YSZ [$(Zr_{0.92}Y_{0.08})O_{1.96}$] were used for measurement of gas sensing ability. Each sample was placed in a fabricated assembly as shown in the following figure:

Figure 3: Fabricated sensor assembly

Change in resistance was measured using digital multimeter. The assembly was injected with increasing concentration of gas like O_2, CO_2, NH_3, NO_x, acetone, alcohol and hydrocarbon oil with the help of a syringe (Dispovan, 5ml). The time required for saturation of signal varied from 10ms to 100ms for various gases. The following graph represents response given by YZOX, YZCT and YZOH with nitrous oxide (NO) with respect to concentration.

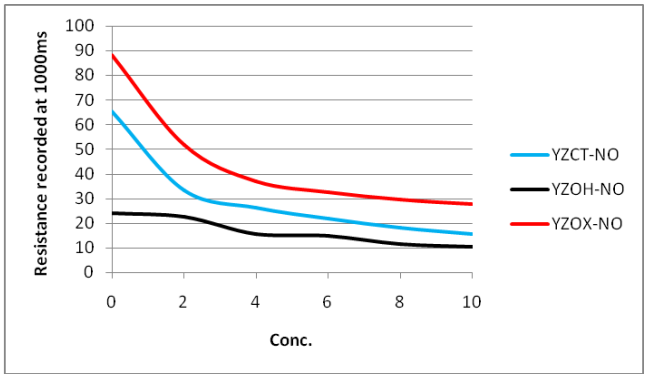

Figure 4: Response of samples to NO

The minimum or maximum responses given by YZOX, YZOH and YZCT for various gases are tabulated below:

Table 1: Responses recorded for various gases

Gases used	YZOX	YZOH	YZCT
O_2	Response saturates at low conc.<2ppm	Comparable and high response	
CO_2	Response saturates at low conc.<2ppm of CO2		
NO	High response	Nonlinear and low	High response
Acetone	High response	No response	
Alcohol	High response	No response	
NH_3	High response	Minimum response	Moderate response
Hydro-carbon oil	Responsive at low conc. < 2ppm. At high conc. sensitivity drops.		

The values are reproducible. This was checked by heating the samples at 100^0C for two hours; furnace cooled and was checked for sensitivity the next day.

Conclusion

- Oxalate is a better precursor for synthesis of 8-YSZ by co-precipitation method.
- It gives stabilization of 8-YSZ in tetragonal crystal structure which is desirable.
- Hydroxide precursor is not suitable for synthesis of partially stabilized 8-YSZ as the product is not free from monoclinic phase.
- Oxalate precursor results into porous 8-YSZ which is sensitive to oxidizing, reducing as well as neutral gases hence best suited for sensor applications.
- The response saturates quickly at about 10 ms and saturates at lower concentration like 2 ppm. This shows better sensitivity at lower concentrations.

The present work will be extended for few other gases, higher temperature sensitivity studies, to check reproducibility and use of neural network for enhancing the reliability of the results.

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