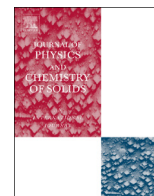




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## Enhancing the phase stability and ionic conductivity of scandia stabilized zirconia by rare earth co-doping

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## ABSTRACT

Effect of co-doping Yb, Gd and Ce in scandia stabilized zirconia (SSZ) on the phase stability, high temperature aging behavior and ionic conductivity was studied. Both binary (10 mol% SSZ) and the ternary (co-doped) compositions were found to be in single cubic phase in the as-processed condition. However, the binary composition exhibited the rhombohedral ' $\beta$ ' phase after sintering whereas the ternary compositions remained in the single cubic phase. The sintered pellets were aged at 900 °C for 500 h in air to study the phase stability at high temperature. Transmission electron microscopy revealed that the aged samples of Yb and Gd co-doped compositions contain small amount of the tetragonal phase which resulted in considerable degradation in conductivity (more than 20%). The Ce co-doped sample, on the other hand, was in single cubic phase after aging and this ensured that conductivity reduction was minimal in this composition. The co-doped samples however, showed higher conductivity before and after aging compared to the binary composition. The rhombohedral ' $\beta$ ' phase was absent in all the co-doped ternary compositions even after high temperature aging.

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## 1. Introduction

In the present world of ever increasing energy needs and decreasing conventional energy resources, solid oxide fuel cells (SOFC) are potential source of clean, efficient and reliable energy conversion which can meet the future energy needs. Phase stability and a stable ionic conductivity of the electrolyte are important in long term operation of SOFCs. Degradation of properties of fuel cell components because of its high operating temperature and prolonged operating time is a major concern for the realization of the SOFC technology [1–3]. Stabilized zirconia systems which show high conductivity and stability at higher temperatures are widely used as the electrolyte in SOFCs [4]. Doped ceria, barium cerate and strontium titanate based proton conductors, brownmillerite structures containing barium and indium etc are some of the other systems of high research interest as SOFC electrolytes [4–10]. Scandia stabilized zirconia (SSZ) shows the highest conductivity among the zirconia based electrolytes, because of less size mismatch of scandia with the host zirconia lattice [11] and hence, is a promising candidate as SOFC electrolyte. However, scandia stabilized zirconia can exhibit other low conducting phases as the cubic lattice can be easily distorted due to the low elastic interactions. This leads to considerable reduction in conductivity during prolonged operation at high temperatures [11–14].

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Co-doping stabilized zirconia is a widely used strategy to improve the conductivity. Various co-dopants like Y, Yb, Gd, Ce, Ca, Ni, Al etc have been explored by researchers. In co-doping with  $Y_2O_3$ , the conductivity was seen decreasing with the increasing  $Y_2O_3$  content. Addition of alumina also showed a decrease in overall conductivity [15–17]. Co-doping with Ce, Ca and Gd was studied with total dopant concentration to be 10 mol%. All the co-dopants were effective in forming single cubic phase [18]. Ce co doping showed highest conductivity followed by Gd and Ca. Addition of Ga was found to be effective in stabilizing the cubic field and improving the conductivity [19]. Addition of Ni showed a decrease in conductivity [20]. Phase stability and ionic conductivity during high temperature exposure was not studied in these studies. It is interesting to note that phase formation and aging behavior of SSZ strongly depend on processing routes [22,23].

In our previous study we demonstrated that the co-doping approach can be adapted effectively to enhance the phase stability of SSZ during processing [21].  $Yb_2O_3$  was chosen as the co-dopant in that study. Co-doping with  $Yb_2O_3$  proved to be effective in improving the stability of the cubic field and enhancing the conductivity in the sintered pellets. However, due to the metastable nature of the phases in stabilized zirconia, it is necessary to investigate the phase stability and conductivity after exposure to high temperatures. The objective of the present investigation is to study the effect of co-doping in SSZ on the phase stability during high temperature exposure and its effect on the conductivity. 9 mol% scandia stabilized zirconia is co-doped with 1 mol%  $Yb_2O_3$ ,  $Gd_2O_3$  and  $CeO_2$  to

improve the stability of the cubic phase and prevent formation of any other low conducting phases so as to reduce high temperature aging of SSZ. The choice of the co-dopants is based on the fact that  $\text{Yb}_2\text{O}_3\text{-ZrO}_2$  and  $\text{Gd}_2\text{O}_3\text{-ZrO}_2$  binary systems do not show any rhombohedral ( $\beta$ ) phase [24] and large atoms like Ce will prefer 8-fold coordination thereby stabilizing the cubic phase [25]. The chosen composition of 9 mol% of scandia and 1 mol% of co-dopant (total 10 mol%) is to ensure that the total dopant concentration lies near the cubic phase field boundary.

Combustion synthesis is a simple, cost effective and fast technique to produce very fine and highly crystalline ceramic oxides [26,27] and is an effective technique to synthesize multi-component systems including SSZ [12,17,21]. Therefore, combustion synthesis was used in the present study to process the binary (SSZ) and ternary (co-doped) compositions. The sintered pellets were subjected to high temperature aging at 900 °C for 500 h and were characterized by X-ray diffraction, electron microscopy and impedance spectroscopy.

## 2. Experimental procedure

### 2.1. Powder synthesis

Combustion synthesis technique was used to process the powders of chosen binary and ternary compositions. The starting materials used were the nitrate salts, zirconium oxynitrate  $\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Sigma aldrich), scandium nitrate  $\text{Sc}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Alfa aesar), ytterbium nitrate  $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (Alfa aesar), gadolinium nitrate  $\text{Gd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (Alfa aesar) and cerium nitrate  $\text{Ce}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (Alfa aesar). The fuel used for the combustion reaction was glycine ( $\text{NH}_2\text{CH}_2\text{COOH}$ ).

Stoichiometric amounts of these starting materials were calculated based on the thermo-chemical concepts used in propellant chemistry [12,21]. Required amount of salts and the fuel were mixed in a silica basin and dissolved in deionised water. Polyethylene glycol was added to the solution as a dispersant. The solution was heated up to 250 °C on a hot plate until a thick viscous solution is formed. The basin was then transferred to a preheated furnace at 600 °C. Combustion took place in the furnace which lasted for only a few minutes with the appearance of fumes. Dry, fragile, foamy powders were formed which were converted to fine powders by manual crushing. The binary composition was 10 mol%  $\text{Sc}_2\text{O}_3$  stabilized zirconia (SSZ) and 1 mol% of ytterbia, gadolinia and ceria was co-doped separately in 9 mol% scandia stabilized zirconia to produce the ternary  $(\text{ZrO}_2)_{0.90}(\text{Sc}_2\text{O}_3)_{0.09}(\text{Yb}_2\text{O}_3)_{0.01}$  (Yb-SSZ),  $(\text{ZrO}_2)_{0.90}(\text{Sc}_2\text{O}_3)_{0.09}(\text{Gd}_2\text{O}_3)_{0.01}$  (Gd-SSZ) and  $(\text{ZrO}_2)_{0.90}(\text{Sc}_2\text{O}_3)_{0.09}(\text{Ce}_2\text{O}_3)_{0.01}$  (Ce-SSZ) compositions respectively.

The resulting fine powders were calcined at 800 °C for 1 h in air to remove the carbonaceous residues. In order to break the agglomerates, the as-processed powders were ball milled after calcination in a Fritsch planetary ball mill for 4 h using zirconia balls at 300 rpm in terpineol medium. The ball to powder ratio was taken as 20:1. The milled powder was dried over night in air at 150 °C. Dried and milled powders were compacted in to pellets in a 12 mm diameter die followed by sintering at 1300 °C for 4 h in air inside a tubular furnace. The density of the sintered pellet was measured using Archimedes' principle.

In order to evaluate the high temperature stability, the sintered pellets were aged at a temperature of 900 °C for 500 h in a tubular furnace in air atmosphere.

### 2.2. Characterization

Phase analysis was performed by X-Ray diffraction on all as processed powders, calcined powders, sintered pellets and aged

pellets on a PANalytical X'Pert PRO diffractometer with  $\text{CuK}\alpha$  ( $\lambda=0.154$  nm) radiation with a step size of  $0.02^\circ$  and a scan rate of 30 s/step.

The pellets were polished and thermally etched at 1250 °C for five minutes for scanning electron microscopy. Observations were made in an HR SEM (FEI Inspect F). For TEM analysis, thin slices were cut from the pellets by diamond saw wheel and polished down to 100  $\mu\text{m}$  using emery paper and subsequently thinned down to 60  $\mu\text{m}$  using a disc grinder (Gatan disc grinder model 623). Samples were then ion milled (Gatan precision ion polishing system model 691) and were observed in a Philips CM12 TEM at 120 kV.

### 2.3. Electrical conductivity measurement

The ionic conductivity of the sintered pellets before and after aging was measured as a function of temperature from 400 °C to 1000 °C at an interval of 50 °C using a Solatron 1260 impedance analyzer in the frequency range of 0.1 Hz to 1 MHz. Platinum paste was used on both sides of the sample for electrical contact and electrical connection was made with two platinum wires. The dimensions of the pellets were measured carefully before each measurement.

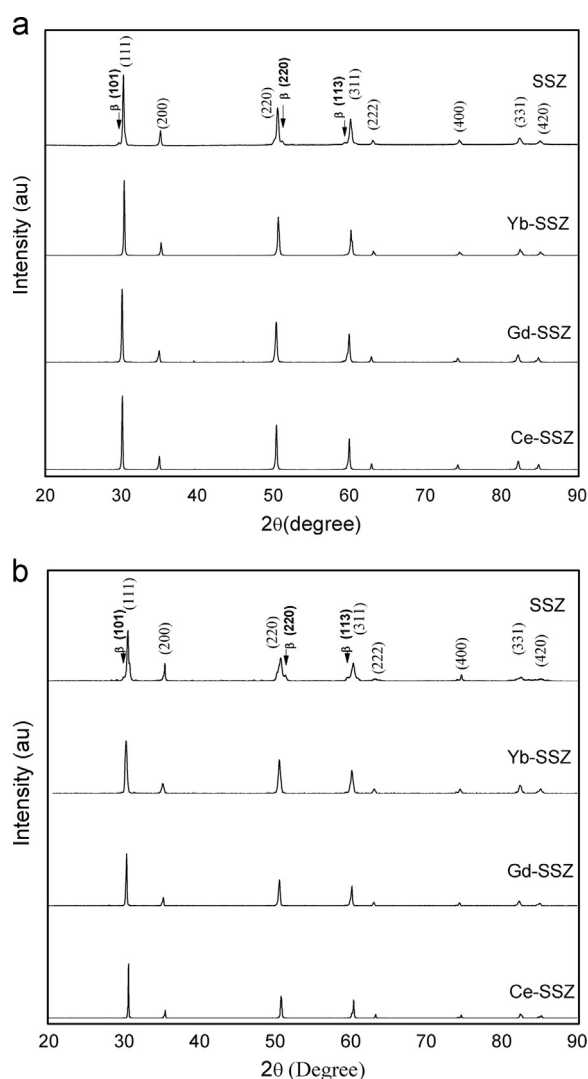


Fig. 1. XRD patterns of samples (a) before aging (as sintered) and (b) after aging.

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