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Preparation of 15 mol% $YO_{1.5}$-doped ThO_2 disk electrolytes by a polymeric gel-combustion method

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Abstract

A hybrid of polymeric gel and auto-combustion techniques was adapted for the synthesis and lower temperature sintering of 15 mol% $YO_{1.5}$-doped thoria (15 YDT) homogeneous solid solutions at 1350°C. The YDT discs so prepared were of density better than 99% theoretical and the cubic cell parameter was $a_o = 558.15(\pm 0.13)$ pm in close agreement with 557.8 pm recently reported as high quality data in JCPDS confirming the validity of the anion vacancy model for $Th_{0.85}Y_{0.15}O_{1.925}$.

1. Introduction

It is well known that the fluorite-structured solid solution of thoria doped with 10–15 mol% $YO_{1.5}$ (10–15 YDT) can be used as a purely oxygen ion conducting solid electrolyte in oxygen potential measurements with their lower electrolytic domain boundary (for 99% or better ionic conduction) extending below that of stabilized zirconia by several orders especially at temperatures above 800°C [1–4]. Subbarao et al. [1] reported the ionic conductivity of YDT to exhibit the maximum at a dopant concentration of about 15 mol% $YO_{1.5}$ at 1000°C. For the formation and sintering of YDT solid solutions, Hund and Mezger [5] resorted to calcining co-precipitated hydroxides in vacuum up to 1800°C to find the solubility limit of $YO_{1.5}$ lying in the range 22–33 mol%. The solubility limits of not only $YO_{1.5}$ but also of other $MO_{1.5}$ (where M = La, Nd, Sm, Gd, Dy, Ho or Er) in the fluorite-type cubic ThO_2 over the range 1500–3200°C were reported by Sibieude and Foex [6] who employed conventional ceramic routes. However, Subbarao et al. calcined co-precipitated nitrates obtained by their aqueous mixture followed by sintering at 2200°C in vacuum to elucidate the solubility curve from 1400–2200°C. Thus, the temperature of the order of 1800–2200°C was required for the sintering of polycrystalline solid solutions of YDT. Recently, lower temperature sintering of thoria and urania–thoria solid solutions were reported in the literature [7,8] by adapting polyvinyl alcohol (PVA) or urea combustion techniques. In the present investigation, a hybrid of polymeric gel [9] and citrate combustion [10,11] designated as 'polymeric gel-combustion' (PGC) method was adapted for the lower temperature synthesis of 15 YDT which was demonstrated to sinter to better than 99% theoretical density at 1350°C.

2. Experimental

2.1. Materials

Reagent grade thorium nitrate hexahydrate (better than 99.99%, Johnson Matthey, UK) and Y_2O_3 (better than 99.99%, IRE, Alwaye, India) were the main starting materials. The other chemicals used were citric acid (99.8%, Merck, India), ethylene glycol (99.9%, Fischer, India) and nitric acid (99.8%, IDPL, India).

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2.2. Procedure

Required quantities of thorium nitrate hexahydrate and Y_2O_3 were separately dissolved in hot water and in 50% excess of warm 1:3 HNO_3, respectively. These solutions were then carefully added to the hot ester, which in turn was prepared by heating an equimolar mixture of citric acid and ethylene glycol. The heating was accompanied by constant stirring up to 90°C for 1–2 h. By heating the syrupy liquid which consisted of a mixture of the ester and nitrate in the mole ratio of 10:1 with excess of citric acid, the temperature was gradually raised to 350°C and maintained for 3–4 h. The colour of the viscous solution gradually changed from yellow to red followed by setting to a brown-coloured, but a transparent glassy gel. On further heating at 500°C for an hour, the gel charred into a powdery resinous mass and finally a black solid mass (referred to as 'precursor') was obtained.

Subsequently, the precursor powder was compacted into cylindrical discs of dimensions 15mm diameter and 5mm thickness at a pressure of 180 MPa. These were sintered in a Pt-wire wound tubular furnace by gradually heating to 1350°C at a rate of 5°C per minute under a cover of purified argon for 20 h. Argon was purified by passing through the various columns of suitable drying agents and oxygen getters. Then, gradual cooling was manually carried out to avoid cooling rates in excess of 10°C min^{-1} down to 800°C. This was followed by natural furnace cooling to room temperature.

Thermogravimetric analysis (TG) of precursor was carried out by using a TG-DTA system, Model Seiko-320 at a heating rate of 10°C min^{-1} in static air. Structural characterization of sintered-15 YDT disc was carried out after pulverizing a disc into fine powder. The powder X-ray diffraction (XRD) pattern was recorded with Cu-Kα radiation using a Rigaku model-miniflux diffractometer, calibrated with a Si standard. The density of 15 YDT discs was determined by pycnometry using dibutyl phthalate. Since the density of dibutyl phthalate itself should be a function of its purity and moisture content, its specific gravity was deduced by using a single crystal of CaF_2 as the standard (with the density of 3.180 Mg m^{-3}) as reported in the literature [12].

For the estimation of porosity, the use of a scanning electron microscope (SEM), Philips SEM model 501 was resorted to. The specimen was initially polished with SiC paper up to 600 mesh followed by polishing with diamond paste. It was then ultrasonically cleaned using acetone followed by plating with gold to facilitate SEM analysis.

3. Results and discussion

In this PGC method, formation of a polymeric gel by the reaction between the citric acid and ethylene glycol ensures homogeneous distribution of tetravalent Th^{4+} and trivalent Y^{3+} ions in the gel matrix thereby precluding their segregation. The presence of suitable excess of nitrate serving as an oxidant facilitated auto-combustion of the citrate-excess polymeric gel (fuel) and hence would help to avoid excessive heating. The gelation process could be followed by the colour changes from colourless transparent gel through brown and red corresponding to the dehydration and decarboxylation reactions of excess citric acid [13].

The simultaneous TG-DTA run taken on the product obtained by slow evaporation of the citrate–nitrate polymeric gel at 350°C is shown in Fig. 1. Though the TG run was extended to 1200°C, constant weight was found to be reached by 550°C after exhibiting nearly 45% weight loss from the ambient. Based on these calculations the temperature of firing of the powder for the complete removal of organics and nitrates was found to be 600°C. This pre-heating of the powder to about 50° higher than the minimum temperature of 550°C recorded by TG was thought to be essential for making the product less bulky and hence, a higher degree of compaction could then be achieved. Attempts made to sinter at intermediate temperatures of about 1000°C did not result in any significant reduction in the dimensions of the disc. However, sintering at 1350°C for a long time was found to be adequate.

A typical XRD pattern recorded after sintering the 15 YDT discs at 1350°C is shown in Fig. 2. For an accurate evaluation of the fluorite cubic cell edge a_o, a Nelson–Riley–Sinclaire (NRS) extrapolation function was made use of and the value of a_o was found to be 558.15($\pm$0.13) pm. This value is in good agreement with 557.8 pm reported in the JCPDS as high quality data after Pfoertsch and Mc Carthy [14] and in fair agreement with 557.6 pm by Hund and Mezger [5] and with 557.0

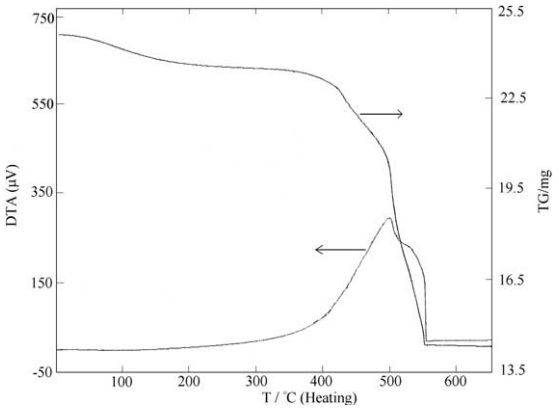

Fig. 1. A TG/DTA analysis of the precursor product obtained by slow evaporation of citrate polymeric gel Th–Y nitrates mixture; ref: α-alumina; sample weight: 24.89 mg. Differential thermocouple: Type S.

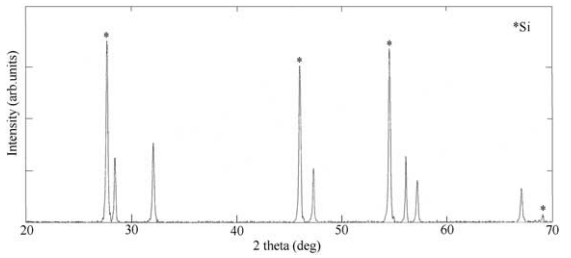

Fig. 2. Powder XRD pattern of 15 YDT (after sintering at 1350°C) using Cu-Kα radiation.

pm reported by Subbarao et al. [1]. Nevertheless, the scatter in the lattice parameter for a constant Y/Th ratio (i.e., 0.15/0.85) would require a careful examination in terms of experimental conditions, defect structure and possible range in oxygen stoichiometry. Significantly lower values of a_o by Hund and Mezger [5] and Subbarao et al. [1] would indicate a higher theoretical density. As their studies involved sintering at temperatures exceeding 2000°C in vacuum, a small fraction of the cations could give rise to cation interstitials leading to higher density (lower a_o value) without affecting the oxygen stoichiometry. The existence of cationic interstitials in a significant proportion was precluded in the present study owing to lower temperature sintering. Further evidence for the anion vacancy model for 15 YDT (without any significant fraction of cation interstitials) could be cited from the recent work reported in JCPDS [15]. This work involved the use of a software programme POWD 12^{++} for the theoretical computations of a_o values for 10, 20 and 30 mol% of YDT based on d values and intensities by Brauer and Gradinger [16] for a single 20 mol% $YO_{1.5}$ solid solution.

These values of fluorite cubic cell edge as a function of mol% of the dopant $YO_{1.5}$ is shown in Fig. 3. The close agreement between the values of 558 (interpolated from Fig. 3 for 15 YDT) and 558.15 pm (this work) upheld the stoichiometry to be $Th_{0.85}Y_{0.15}O_{1.925}$ conforming to the anion vacancy model almost exclusively. For all the compositions, the a_o values reported by Subbarao et al. [1] are consistently lower than the calculated ones as well as those of high quality data reported in JCPDS. The theoretical density as calculated from the present XRD data is 9.2179 Mg m^{-3} which differs insignificantly from 9.2180 Mg m^{-3}. Making use of the value of 3.180 Mg m^{-3} for the density of the single crystal CaF_2, the average specific gravity of dibutyl phthalate was determined using pycnometry to be 1.023 Mg m^{-3} with little exposure of the dibutyl phthalate to the atmosphere. A value of 9.179 Mg m^{-3} was measured as an average density of five discs of 15 YDT. This corresponded to a porosity of about 0.5%. To ascertain the size and distribution of pores, a SEM photomicrograph of YDT discs was recorded at a

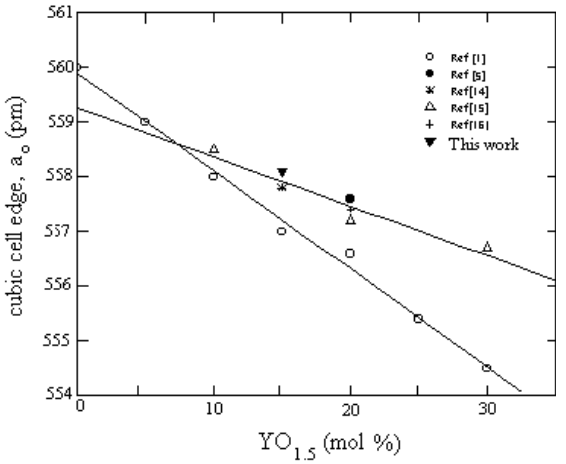

Fig. 3. Variation of the ThO_2 fluorite cell cubic edge with the concentration of $YO_{1.5}$.

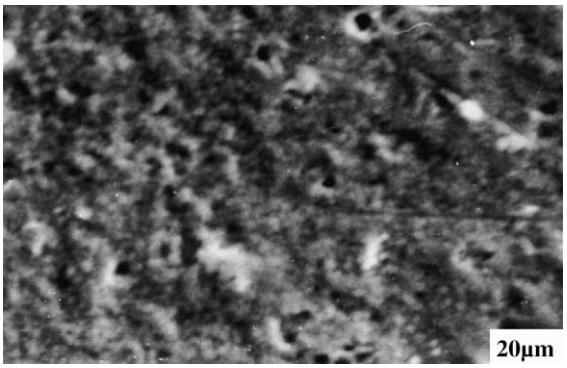

Fig. 4. A SEM photomicrograph of 15 YDT disc.

magnification of 5200× and is shown in Fig. 4. The pores were found to be randomly distributed and are of 6–12 μm in diameter. The observed differences in brightness were due to surface inhomogeneities.

4. Conclusion

The hybrid method reported in this work facilitates the preparation of high density, better than 99% theoritical density discs of 15 mol% $YO_{1.5}$-doped thoria at sintering temperatures as low as 1350°C and with a defect structure conforming to the anion vacancy model based on X-ray density considerations.

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