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Stabilization of the cubic phase in zirconia–scandia by niobium oxide addition



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ABSTRACT

Zirconia–10 mol% scandia (ScSZ) with additions of x mol% niobium oxide ($x=0, 0.25, 0.5$ and 1) nanoparticles were chemically synthesized. The introduction of niobium as a codopant is proposed for stabilization of the cubic phase of zirconia–scandia solid electrolyte. Several compositions were synthesized by a solution method to ensure chemical homogeneity. The thermal analysis results reveal that the addition of niobium oxide reduced the crystallization temperature of zirconia. The morphology of the calcined powders consists of agglomerated nanoparticles with 6.5 nm mean crystallite size. *In situ* high-temperature X-ray diffraction evidenced the full stabilization of the cubic phase of zirconia–10 mol% scandia containing 0.5 mol% niobium oxide content.

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1. Introduction

Zirconia-based solid solutions are functional materials widely used as solid electrolytes for a number of technological applications including solid oxide fuel cell devices and oxygen sensors [1,2]. The scandia-doped zirconia solid electrolyte exhibits the highest ionic conductivity value among stabilized zirconias [1,2]. The main concern with respect to this system is the stabilization at room temperature of the high ionic conductivity cubic phase for scandia contents in the 9.5–13 mol% range. This stabilization avoids the formation of the low ionic conductivity β rhombohedral phase [3]. The reversible (cubic– β rhombohedral) first order phase transformation occurs at 600 °C during heating. The main approach to suppress this phase transformation has been the introduction of a codopant.

Several oxides have been proposed for that purpose, such as Al_2O_3 [4], Gd_2O_3 [5], CeO_2 [6], Y_2O_3 [7], Yb_2O_3 [8], In_2O_3 and Sm_2O_3 [9], and Dy_2O_3 [10]. The addition of these oxides has proved to be efficient, to some extent, for stabilizing the cubic phase in the zirconia–scandia solid electrolyte. In most of those studies, the ternary solid solutions were prepared by the conventional method of mixing the starting oxides followed by solid state reactions at high temperatures [4,6,7,9]. This method has the advantage of large scale production, but the overall stoichiometry of the product material may be compromised, mainly when the codopant is introduced in very small contents [11]. Solution methods of

synthesis are characterized by a complete and homogeneous mixing of the starting ingredients at molecular level, thereby the stoichiometry of the final material is preserved [12]. In addition, the use of a solution method is known to yield powder particles in the nanosize range, with improved properties comparing to microcrystalline powders.

This report presents for the first time the stabilization of the cubic phase of zirconia–10 mol% scandia with a pentavalent cation, Nb^{5+} . The choice for niobium was due to its ionic radius (0.74 Å [13]) close to that of Zr^{4+} (0.84 Å [13]) in 8-fold coordination. The similarity between the ionic radii is expected to favor solid solution formation and to minimize the elastic strain energy due to ionic mismatch. The studied compositions were prepared by a facile solution method to ensure a suitable chemical homogeneity, and the effects of the additive on the thermal, structural and microstructural characteristics of the parent solid electrolyte were investigated.

2. Experimental

Preparation of the nanoparticles: Zirconyl nitrate (99.9%, Aldrich, USA), scandium nitrate (99.9%, Alfa Aesar, USA) and niobium ammonium oxalate (99.99%, CBMM, Brazil) were used as starting materials. The synthesized compositions were ZrO_2 –10 mol% Sc_2O_3 – x mol% Nb_2O_5 with $x=0, 0.25, 0.5$ and 1.0 . The several compositions were prepared by the hydroxide coprecipitation method followed by azeotropic distillation.

Stock solutions of the starting materials were prepared with deionized water. Ammonium hydroxide of analytical grade was used as the precipitant agent. The concentration of the stock solution was

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determined by gravimetry. The pH of the precipitation solution was controlled throughout the experiments within 9–10 and the concentration of the cation solution was fixed at 0.1 mol L^{-1} . After precipitation completion, the gel was separated from the mother liquid by centrifuging at 2800 rpm for 5 min. Afterwards, the gel was washed several times with water, absolute ethanol and isopropyl alcohols before the azeotropic distillation with *n*-butyl alcohol. After the washing and dewatering processes, the gel was dried at $50 \text{ }^\circ\text{C}$ in an oven for 48 h. The dried precipitate was deagglomerated in an agate mortar and calcined at $500 \text{ }^\circ\text{C}$ for 2 h with heating rate of $2 \text{ }^\circ\text{C min}^{-1}$.

Characterization methods: Thermal characterization of the as-prepared material was carried out by simultaneous thermogravimetry, TG, and differential thermal analyses, DTA (STA 409, Netzsch) from room temperature to $1100 \text{ }^\circ\text{C}$ with heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ in synthetic air (5 mL min^{-1}). Alpha alumina was used as the reference material. The morphology of the calcined particles was observed by transmission electron microscopy (Jeol, JEM 2100). Phase characterization was performed in the calcined material by X-ray diffraction analysis (Bruker-AXS, D8 Advance, Cu K_α radiation) in the $20\text{--}80^\circ 2\theta$ angular range, with 0.05° step size and 2 s time per step. The crystallite size was estimated using the Scherrer equation for (111) reflection of the cubic phase. High temperature X-ray diffraction, HTXRD, was carried out on powder specimens containing 0.25 and 0.5 mol% niobia from room temperature to $700 \text{ }^\circ\text{C}$ in a diffractometer (Bruker-AXS, D8 Advance) with Bragg-Brentano $\theta\text{--}\theta$ geometry, equipped with a Braun position sensitive detector and a heating stage (Antor Paar HTK 1400). For these experiments, the powder material was pressed into pellets, sintered at $1450 \text{ }^\circ\text{C}$ for null holding time and, after cooling down to room temperature it was ground into a fine powder. Data were collected at selected temperatures in the $47\text{--}54^\circ 2\theta$ range in 0.073° steps.

3. Results and discussion

Fig. 1 shows TG and DTA curves of the dried as-prepared nanopowder containing 1 mol% niobia. The weight loss occurs up to approximately $450 \text{ }^\circ\text{C}$ and is accompanied by an endothermic event at $110 \text{ }^\circ\text{C}$ and two exothermic events at 280 and $430 \text{ }^\circ\text{C}$. The endothermic event is assigned to physisorbed water evidencing the hygroscopic nature of the as-prepared material; the exothermic peak at $280 \text{ }^\circ\text{C}$ is related to the mixed hydroxide decomposition; the $430 \text{ }^\circ\text{C}$ exothermic peak is attributed to the crystallization of the solid solution. It was previously shown that pure zirconia

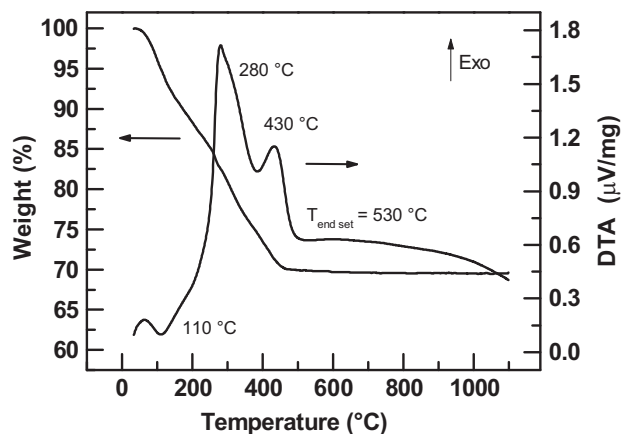


Fig. 1. TG and DTA curves of the as-prepared nanopowder of zirconia–scandia with 1 mol% niobia.

synthesized by the same method crystallizes at $447 \text{ }^\circ\text{C}$ [14]. Hence, this result shows that the niobium oxide promotes the reduction of the crystallization temperature of zirconia.

Fig. 2a depicts the X-ray diffraction pattern of the calcined nanopowder with 1 mol% niobia. This pattern was indexed with the JCPDS file 89-5483 corresponding to the cubic structure of zirconia. The broad diffraction peaks are in agreement with the low crystallite size determined by the Scherrer equation and amounts to 6.5 nm after calcination at $500 \text{ }^\circ\text{C}$.

The nanostructured nature of the synthesized ScSZ nanopowder with 1 mol% niobia is shown in the TEM micrograph (Fig. 2b) obtained after calcination at $500 \text{ }^\circ\text{C}$. Agglomerated nanoparticles may be seen. The inset shows a high magnification micrograph of a microregion.

Fig. 3 shows powder HTXRD patterns for ScSZ containing (a) 0.25 and (b) 0.5 mol% niobia heat treated at $1450 \text{ }^\circ\text{C}$.

The angular range ($47\text{--}54^\circ$) corresponds to that where the cubic and the rhombohedral phases are unambiguously identified. The (220) reflection of the cubic phase is indicated in these patterns. The HTXRD patterns of the specimen with 0.25 mol% niobia (Fig. 3a) exhibit the characteristic reflections of the β -rhombohedral phase up to $400 \text{ }^\circ\text{C}$. This means that, this small amount of codopant partially stabilizes the cubic phase and reduces the temperature for the rhombohedral–cubic phase transformation, which is around

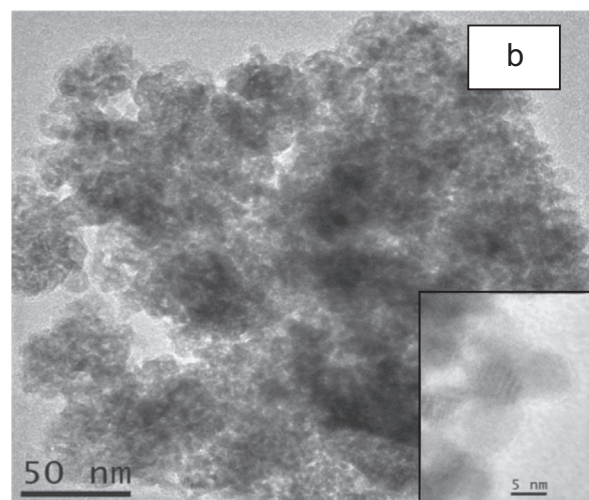
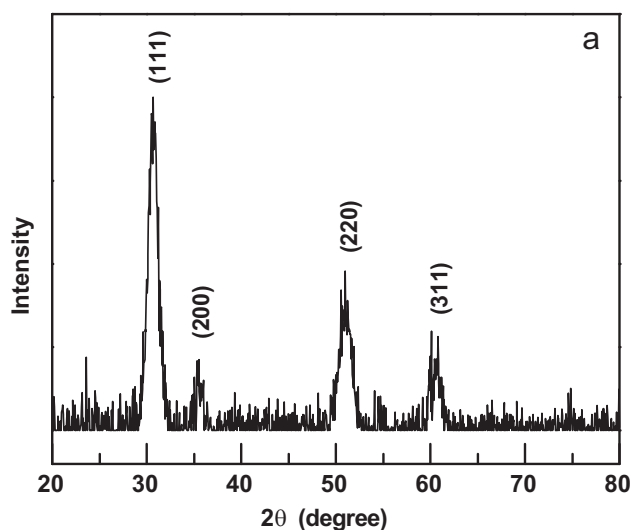


Fig. 2. (a) X-ray diffraction pattern and (b) TEM micrograph of the nanopowder of zirconia–scandia with 1 mol% niobia calcined at $500 \text{ }^\circ\text{C}$ for 2 h. Inset: high magnification TEM micrograph.

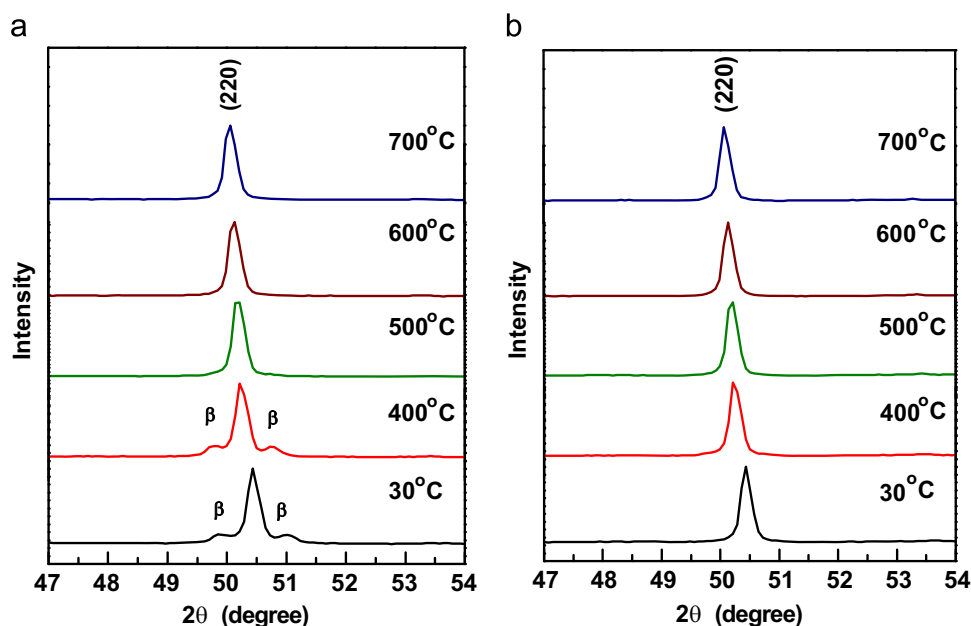


Fig. 3. *In situ* powder HTXRD patterns from room temperature to 700 °C of (a) 0.25 and (b) 0.5 mol% niobia after heat treatment at 1450 °C.

600 °C in zirconia–10 mol% scandia [3]. Fig. 3b shows the HTXRD patterns of the specimen with 0.5 mol% niobia. In this case, the single detected reflection corresponds to that of the cubic structure evidencing total stabilization of the high symmetry structure. The lattice parameters at room temperature calculated using the Unicell software are 5.085 and 5.081 Å, respectively, for specimens with 0.25 and 0.5 mol% niobia. A more extensive study on the stabilization of the cubic phase and the electrical properties of these compounds will be separately published.

4. Conclusions

Zirconia containing scandia and niobia was successfully synthesized by a solution route. Nanopowders with mean crystallite size of 6.5 nm were obtained after calcinations at 500 °C. After heat treatment at 1450 °C, full stabilization of the cubic phase at room temperature was obtained for niobia addition of only 0.5 mol%. The synthesized material is a potential candidate as solid electrolyte for application in solid oxide fuel cells operating at intermediate temperature.

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