

Evaluation of the effect of heavy rare earth elements on electrical resistivity of zirconia-yttria ceramics

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Abstract. The use of yttria concentrates was investigated in this study for synthesis and processing of zirconia based ceramics applied as solid electrolyte materials. Terbium, dysprosium, holmium, erbium and ytterbium are the chemical elements, classified as heavy rare earths, that can be found in those concentrates due to their association with yttrium ores. The ceramic characteristics were compared to zirconia-yttria and zirconia-yttria-heavy rare earth oxide systems, containing 3 and 9 mol% of dopant. Powders were prepared by the coprecipitation route and ceramic processing conditions were established to attain relative densities up to 95%. The characterization of as-sintered pellets was performed by apparent density measurement by Archimedes method, X-ray diffraction, scanning electron microscopy and electrical resistivity measurement by impedance spectroscopy. It was observed that the presence of heavy rare earths in a concentrate containing 85 wt% of yttria has no significant influence on the total ionic resistivity of zirconia based ceramics.

Introduction

Yttria is an oxide commonly used to stabilize the cubic and tetragonal phases of zirconia, at room temperature, preventing the tetragonal \rightarrow monoclinic phase transformation of pure oxide, which occurs at 1150 °C with a disruptive volume change. Stabilization is accomplished by a partial substitution of Y^{3+} ions for the host lattice cation (Zr^{4+}), creating oxygen vacancies that result to a high ionic conductivity over a wide range of temperature and oxygen pressure. This feature has led zirconia-yttria ceramics suitable for applications as solid electrolytes in electrochemical devices for energy conversion in solid oxide fuel cells and for oxygen determination in steel melts and automobile exhaust [1,2].

It is well known that the maximum in conductivity for zirconia-yttria ceramics is attained at elevated temperatures (\sim 1000 °C) close to the lower limit for fully stabilization of cubic phase, that can be formed with the addition of 8-9 mol% Y_2O_3 [3]. Recently, the development of nanosized materials has shown that zirconia ceramics doped with 2,5-3 mol% Y_2O_3 could also be considered as a promising solid electrolyte [4-6]. This material, commonly referred as yttria-tetragonal zirconia polycrystals (Y-TZP), has remarkable mechanical properties [7] and could achieve higher ionic conductivity in the low temperature domain (400-700 °C), compared to cubic stabilized zirconia (CSZ). The greatest limitation of Y-TZP ceramics is the degradation of mechanical properties in humid environments at relatively low temperatures (200-300 °C) due to the formation of monoclinic phase at the ceramic surface [8]. Besides the dopant concentration, the ionic conductivity is also a function of valence and size of dopant cation [3]. Dopants that can easily change their oxidation state may introduce electronic conductivity on the material (ex. Tb_4O_7) and larger dopant cations can block the migration of vacancies decreasing ionic conductivity [9-11].

In this work, it was evaluated the influence of heavy rare earths oxides, remaining in yttria after an intermediate purification step [12], on the resistivity and microstructure of zirconia-yttria solid electrolyte. For this purpose, zirconia ceramics were prepared from powders doped with 3 and 9 mol% of high purity yttria or concentrates containing 85 and 95 wt% of this oxide.

Experimental Procedure

Zirconium oxychloride (IPEN, Brazil) and rare earth chlorides, prepared by solvent extraction [12] and hydrochloric dissolution of 99,9 % Y_2O_3 , Tb_4O_7 , Dy_2O_3 , Er_2O_3 , Ho_2O_3 and Yb_2O_3 (Aldrich, USA), were the precursor solutions used in this work. The chemical composition of yttria concentrate prepared by solvent extraction is shown in Table 1.

Table 1: Chemical composition, determined by X-ray fluorescence analysis, of M1 yttria concentrate prepared by solvent extraction.

Sample code	Composition (weight %)						
	Y_2O_3	Dy_2O_3	Er_2O_3	Ho_2O_3	Yb_2O_3	Tb_4O_7	others
M1	84.4	8.7	4.2	1.9	0.3	0.2	0.3

Stabilized zirconia powders were synthesized by the coprecipitation route [13], according to chemical composition presented in Table 2. M2 concentrate is a synthetic mixture containing 95 wt% of yttria. To verify the influence of individual heavy rare earths, M3 samples simulate the 85 wt% yttria concentrate. It is important to notice that, except for sample 9M3Tb, the molar composition of these samples is very similar due to the similar molecular weight and valence of these rare earth elements. The same molar composition is provided by sample 9M4Tb that was stabilized with a mixture of 74 wt% of yttria and 26 wt% of terbia.

Table 2: Chemical composition of rare earth oxides in stabilized zirconia powders.

Sample code	Composition (mol %)					
	Y_2O_3	Dy_2O_3	Er_2O_3	Ho_2O_3	Yb_2O_3	Tb_4O_7
3P	3.00	—	—	—	—	—
3M1	2.72	0.18	0.04	0.04	<0.01	<0.01
9P	9.00	—	—	—	—	—
9M1	8.10	0.50	0.23	0.10	0.02	0.01
9M2	8.73	0.15	0.08	0.04	<0.01	<0.01
9M3Dy	8.13	0.87	—	—	—	—
9M3Er	8.15	—	0.85	—	—	—
9M3Ho	8.14	—	—	0.86	—	—
9M3Yb	8.17	—	—	—	0.83	—
9M3Tb	8.56	—	—	—	—	0.46
9M4Tb	8.13	—	—	—	—	0.87

Calcined and milled powders were pressed by uniaxial compaction (100 MPa) and sintered in air at 1500 °C for 1 hour. The apparent densities of as-sintered pellets were determined by Archimedes method. Microstructural observations were carried out on polished and thermally etched ceramic surfaces, by scanning electron microscopy (XL30, Philips) and grain size was estimated by Quantikov image analysis [15]. Quantitative phase analysis and determination of theoretical density were performed by Rietveld refinement of X-ray diffraction patterns (DMAX2000, Rigaku). Electrical impedance spectroscopy measurements (HP4192A, Hewlett Packard) were carried out over a wide frequency range (5 Hz to 13 MHz) at temperatures between 250 - 550 °C. For this purpose silver electrodes were applied to the parallel surfaces of sintered samples by painting and baking at 500 °C.

Results and discussion

Rietveld refinement results and the apparent density of as-sintered pellets are shown in Table 3. It can be observed the predominance of the tetragonal phase for zirconia ceramics doped with 3 mol% of rare earth oxides (3P and 3M1 samples). In this case the occurrence of monoclinic phase may be a consequence of the transformation – toughening phenomena during cooling and/or polishing procedures. The addition of 9 mol% of rare earth oxides stabilizes the cubic phase. Apparent densities higher than 95% of the theoretical values were achieved for all samples.

Table 3: Phase analysis and density values of stabilized zirconia ceramics.

Sample code	Phase composition (wt%)			ρ theoretical (g.cm ⁻³)	ρ aparent (g.cm ⁻³)	% ρ theoretical
	tetragonal	monoclinic	cubic			
3P	96	4	—	6.07	5.92 ± 0.03	97.5 ± 0.5
3M1	96	4	—	6.11	5.96 ± 0.03	97.6 ± 0.5
9P	—	—	100	6.01	5.73 ± 0.02	95.3 ± 0.3
9M1	—	—	100	6.11	5.84 ± 0.03	95.6 ± 0.5
9M2	—	—	100	6.05	5.60 ± 0.09	92.6 ± 1.5
9M3Dy	—	—	100	6.06	5.81 ± 0.03	95.9 ± 0.5
9M3Er	—	—	100	6.07	5.82 ± 0.04	95.9 ± 0.7
9M3Ho	—	—	100	6.07	5.75 ± 0.03	94.7 ± 0.5
9M3Yb	—	—	100	6.07	5.72 ± 0.06	94.2 ± 1.0
9M3Tb	—	—	100	6.03	5.80 ± 0.02	96.2 ± 0.3
9M4Tb	—	—	100	6.05	5.79 ± 0.01	95.7 ± 0.2

Mean grain size values and typical SEM micrographs of polished and thermally etched surfaces of zirconia ceramics doped with 3 and 9 mol% of rare earth oxides are shown in Table 4 and Fig.1, respectively. TZP ceramics (samples 3P and 3M1) have a mean grain size around 0.3 μ m. Similarity in the microstructures was observed for each dopant concentration. The twinning feature of coarser grains pointed out in Fig. 1a is an indication of the existence of monoclinic phase. Probably, these grains transformed during cooling due to the greater grain size [7, 15]. Mean grain size of CSZ ceramics (9P and 9M samples) is in the range of 3 - 5 μ m.

Table 4: Mean grain size of stabilized zirconia ceramics.

Sample code	Mean grain size (μ m)
3P	0.3 ± 0.1
3M1	0.3 ± 0.1
9P	3.8 ± 1.8
9M1	4.6 ± 2.1
9M2	4.1 ± 1.8
9M3Dy	4.6 ± 2.1
9M3Er	3.0 ± 1.4
9M3Ho	3.5 ± 1.6
9M3Yb	4.0 ± 1.9
9M3Tb	4.3 ± 1.9
9M4Tb	4.0 ± 1.8

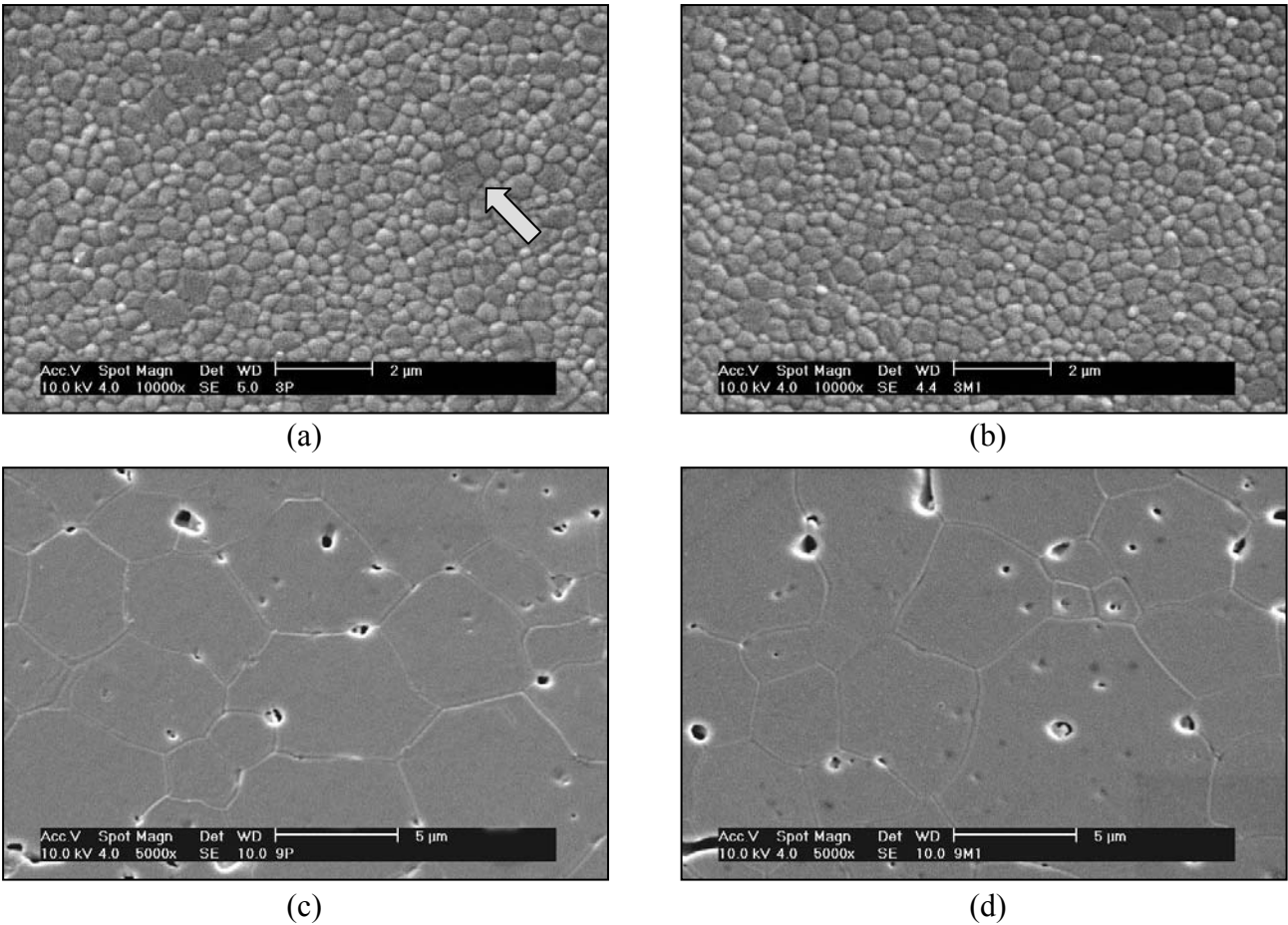


Fig. 1: SEM micrographs of polished and thermally etched surfaces of stabilized zirconia ceramics: (a) 3P, (b) 3M1, (c) 9P and (d) 9M1.

Fig. 2 shows Arrhenius plots of electrical resistivity of all stabilized zirconia ceramics studied in this work. At 400 °C, it was observed that the resistivity of TZP samples is 75–85% higher than the resistivity of CSZ ceramics. Considering that at this temperature intragrain resistivities of TZP and CSZ ceramics are in the same order of magnitude, this behaviour can be explained as a consequence of high grain boundary densities of TZP ceramics [4, 16]. For a fixed dopant concentration, it was verified that the presence of heavy rare earths in yttria concentrate has no significant influence on the total resistivity of zirconia ceramics. As previously observed by Arachi et al. [17], this behaviour is mainly due to the close ionic radius of heavy rare earth trivalent ions: 1.019 Å for Y^{3+} and in the range of 0.98 to 1.04 Å for Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} and Yb^{3+} [18]. The low level of silica, alumina and ions that reduce vacancy concentration also contribute to this feature [19, 20].

The electrical conductivity values of TZP and CSZ ceramics prepared in the present work were compared to the results obtained for ceramics produced from commercial coprecipitated powders (Table 5). In spite of the greater purity level of commercial powders, it can be observed the smaller conductivity of the CSZ material prepared by Ciacchi et al. [16], which is probably a consequence of differences in ceramic processing conditions.

Conclusions

Zirconia ceramics stabilized with yttria concentrates by the coprecipitation route have shown to be promising materials for solid electrolytes applications due the possibility of cost reduction for industrial scale production. A homogeneous microstructure was observed for all samples, with

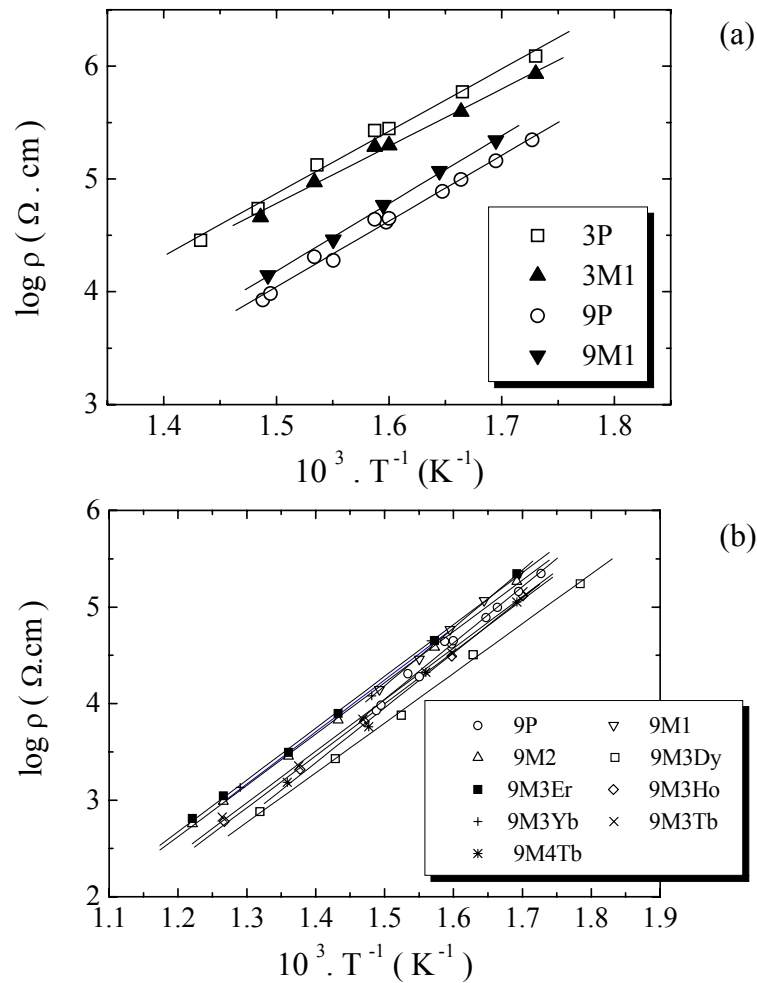


Fig.2: Arrhenius plots for electrical resistivity of stabilized zirconia ceramics: (a) 3P, 3M1, 9P and 9M1 and (b) 9P and 9M samples.

Table 5: Values of activation energy (E) and pre-exponential factor (ρ_0) of ionic conduction process and electric conductivity at 400 °C and 1000 °C (estimated).

Sample code	E (eV)	ρ_0 ($10^{-4} \Omega \cdot \text{cm}$)	$\sigma_{400 \text{ °C}}$ ($10^{-4} \Omega^{-1} \cdot \text{cm}^{-1}$)	$\sigma_{1000 \text{ °C}}$ ($\Omega^{-1} \cdot \text{cm}^{-1}$)
3P	1.10	3.80	0.16	0.12
3M1	1.01	14.60	0.20	0.07
* HS3Y	0.85	83.2	0.54	0.05
9P	1.16	0.20	1.09	1.33
9M1	1.19	0.15	0.80	1.27
9M2	1.05	1.78	0.72	0.38
9M3Dy	1.02	1.20	1.88	0.76
9M3Er	1.06	1.71	0.62	0.36
9M3Ho	1.07	0.85	1.20	0.70
9M3Yb	1.07	1.47	0.68	0.40
9M3Tb	1.06	1.09	1.09	0.59
9M4Tb	1.13	0.30	1.33	1.27
* MEL 8Y	1.01	6.50	0.44	0.16

* Ciacchi et al. [16].

grain size around $0.3\mu\text{m}$ and $4\mu\text{m}$ for TZP and CSZ ceramics, respectively. Activation energy of the ionic conduction process is approximately 1eV. Electrical conductivities values are greater when zirconia cubic phase is stabilized.

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