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Preparation of Gd_2O_3-doped ZrO_2 by polymeric precursor techniques

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Abstract

Zirconia–10 mol% gadolinia was prepared by several techniques involving polymeric precursors: the Pechini, the PVA and the amorphous citrate techniques. The aim of this work is to determine among these techniques the most suitable to obtain solid solutions with high chemical homogeneity and high sinterability. The main results show different paths for decomposition of the polymeric precursors. Calcined powders presented similar particle size distribution curves although they are related with the distribution of agglomerated particles. Agglomerate morphology is also quite different as observed by scanning electron microscopy, and the powder prepared by the citrate (Pechini) technique is found to be chemically inhomogeneous. The PVA technique is the less complex route for solid solution synthesis. The higher densification was obtained for powders prepared by the amorphous citrate technique.

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1. Introduction

ZrO_2-based ceramics can be used as ionic conductors and high-temperature structural materials because they have an excellent combination of electrical, thermal, and mechanical properties. For most of the current applications, a suitable amount of a dopant ion (Mg^{2+}, Ca^{2+}, Y^{3+} or rare earths) must be introduced in the crystal lattice to obtain the desired phase composition [1].

Several procedures may be followed for the preparation of these solid electrolytes including solid, solution or vapor phase methods [2,3]. Solution methods are recognized as relatively simple to perform, low-cost, and effective to produce high surface area powders. These methods are intended to take advantage of the enhanced chemical homogeneity obtained in the solution phase. For this reason, these methods can be classified according to the procedure used to separate the solvent [2]. Some of these methods involve the volatilization of the solvent in vitreous, gelatinous or amorphous matrices. The diffusion rates for cations in

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these matrices are quite low so that the chemical homogeneity of the final powders can be improved. One of the oldest techniques employing this concept is the polymeric precursor technique, also known as the citrate process, developed by Pechini [4] to produce mixed oxides for capacitors and coatings. In that process, an alpha-hydroxycarboxylic acid such as citric acid is used to chelate with various cation precursors forming a polybasic acid. In the presence of a polyhydroxy alcohol, such as ethylene glycol, these chelates will react with the alcohol to form organic esters and water. Heating the mixture, polyesterification occurs yielding a homogeneous sol; metal ions are found to be uniformly distributed throughout the organic matrix in that sol. The crystallization occurs simultaneously with the elimination of the organic matter in a subsequent thermal treatment, giving rise to a crystalline material with high chemical and structural homogeneity. This technique has been used to produce reactive powders of zirconia with different stabilizer: calcia (CaO), ceria (CeO_2), magnesia (MgO), and yttria (Y_2O_3) [5–8].

Another variant of the polymeric precursor technique is the amorphous citrate technique [9]. In this case, citric acid is added to the cation solution forming a gel. Reactive zirconia powders doped with either ceria or yttria have been prepared according to this technique [10].

Recently, the use of polyvinyl alcohol as polymerization agent was suggested due to its comparatively long molecular chain [11]. This technique has proved to be quite simple and effective for preparing a number of compounds [12,13].

Gadolinia-doped zirconia solid solutions have been prepared by several solution techniques as coprecipitation and sol–gel [14], and the polymeric precursor method [15,16]. These techniques usually give rise to high sinter-reactive powders. In the case of this solid solution, however, high sintering temperatures and long soaking times were used in order to attain relative densities larger than 92%.

The aim of this work is to prepare sinter-reactive powders of zirconia–10 mol% gadolinia. Three solution methods employing polymeric matrices have been used for this purpose. The main objective is to determine among these techniques the most effective to obtain rare earth-doped zirconia solid electrolytes nanosized powders with high sinterability.

2. Experimental procedures

2.1. Citrate (Pechini) technique

Hydrated zirconium oxide (>99%, produced at this Institute) and Gd_2O_3 (>99.9%, Alpha Ventron) were used to prepare a nitrate solution containing the cations in the desired proportion. The metallic cation:citric acid and citric acid:ethylene glycol molar ratios were 1:1 and 60:40, respectively. The resin was calcined at 250 °C and subsequently at 800 °C for 1 h.

2.2. Amorphous citrate technique

$ZrOCl_2 \cdot 8H_2O$ (>99%, Becto) and Gd_2O_3 (>99.9%, Alpha Ventron) were used as starting materials. A gadolinium nitrate solution was prepared and mixed with a water solution of zirconium oxychloride. The citric acid:water:metallic ion molar ratio was 12.5:300:1. In this case, increasing the viscosity, a gel is clearly formed before the resin is obtained. The decomposition reaction was performed at 250 °C and 700 °C for 1 h.

2.3. PVA technique

Either hydrated zirconium oxide or zirconium oxychloride together with gadolinium oxide were used as starting materials. The purpose was to verify the main differences using either a nitrate or a chloride as precursor. A 10 wt.% polyvinyl alcohol (Erich, MW 72,000) solution was used to prepare the resin. A 1:2.5 metallic ion:monomer vinyl molar ratio was used. Calcination was carried out at 250 °C and 700 °C for 1 h.

The citrate technique, the amorphous citrate technique and the PVA technique are hereafter named pp, ac and PVA techniques, respectively.

2.4. Characterization

Thermal decompositions of resins were studied by thermogravimetry and differential thermal analysis (STA 409, Netzsch) with a 10 °C min^{-1} heating rate up to 1200 °C and cooling at the same rate under flowing synthetic air. Alumina was used as reference material in DTA runs. Particle size distributions (Granulometer 1064, Cilas) in calcined powders were measured by laser scattering. Values of specific surface area

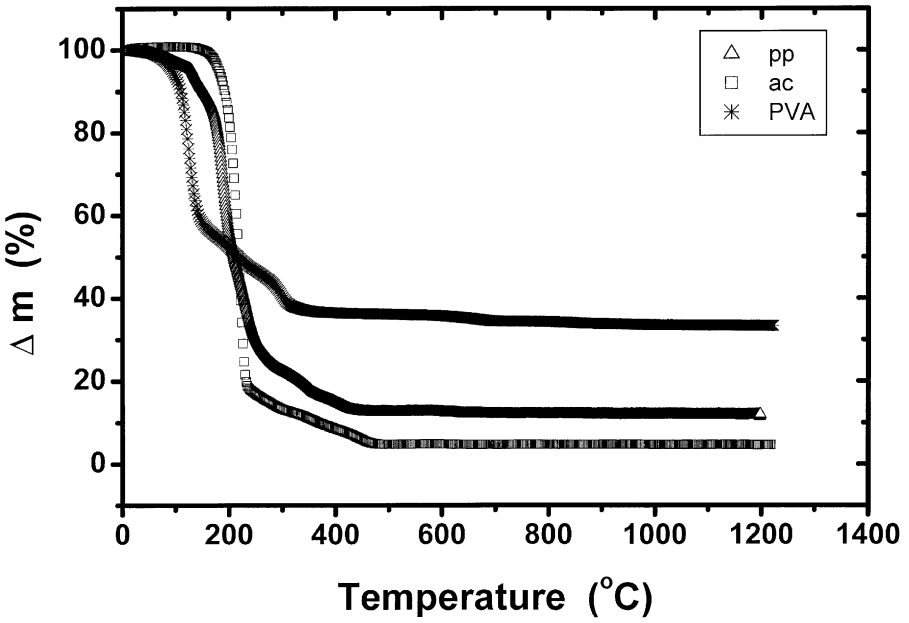

Fig. 1. TG curves of ZrO_2:Gd_2O_3 powders prepared by different chemical techniques: citrate technique (pp); amorphous citrate technique (ac); PVA technique (PVA).

were obtained by nitrogen adsorption (ASAP 2010, Micromeritics) by the BET technique. Particle morphology was observed in a scanning electron microscope (XL 30, Philips). Linear shrinkage was measured by dilatometry (DIL 402 E/7, Netzsch) with 8 and 15 °C min^{-1} heating and cooling rates, respectively.

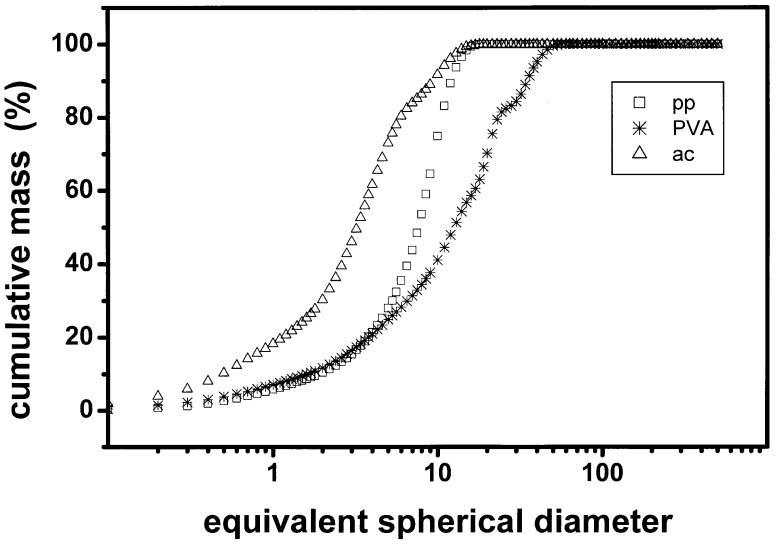

Fig. 2. Particle size distribution curves for ZrO_2:Gd_2O_3 powders prepared by different chemical techniques: citrate technique (pp); amorphous citrate technique (ac); PVA technique (PVA).

3. Results and discussion

Fig. 1 shows the TG curves of the precursor resins. Curves for resins prepared by the citrate and amorphous citrate techniques are similar. The weight loss occurs in two steps for all resins. The first step is related to free water and evaporation of organic compounds. The second step is assigned to a depolymerization reaction. For the resin prepared by the PVA technique, the weight loss also occurs in two steps, but within different temperature ranges. Total weight loss is between 67% and 95%. The weight loss for temperatures higher than 500 °C is negligible although powders calcined at temperatures up to 600 °C present a light gray color assigned to carbon-like residues. The related DTA curves show evidence of thermal effects due to the removal of water and volatile compounds, the decomposition of polyester chain or metal bonded carboxyl, and the elimination of organic matter.

Values of specific surface area of powders prepared according to the three techniques are: 21.2 (pp), 63.8 (ac) and 24.3 (PVA). This result shows that the amorphous citrate technique is the most effective to produce ZrO_2:Gd_2O_3 reactive powders.

Fig. 2 shows particle size distribution curves for all powders prepared according to the techniques described above. The shape of the curves is similar, and the following average particle/agglomerate sizes were determined: 7.64 μm for powders prepared by the polymeric precursor (pp) technique, 3.23 μm for the amorphous citrate (ac) technique, and 12.61 μm for the polyvynil alcohol (PVA) technique.

Scanning electron micrographs for the study of the morphology of the calcined powders are shown in Fig. 3. The citrate technique (top micrograph) produced powders with rounded and acicular particles. These acicular particles were found to have low gadolinium content determined by energy dispersive X-ray analysis. Powders prepared by the PVA technique (middle micrograph) present agglomerated particles, while the amorphous citrate technique (bottom micrograph) produced small rounded particles.

Fig. 4 shows the shrinkage behavior of compacts of powders prepared by the three techniques. The shrinkage of the compact prepared by the amorphous citrate technique starts at a lower temperature than the shrinkage of the other pressed powders. The densification of powder compacts prepared by the citrate and PVA

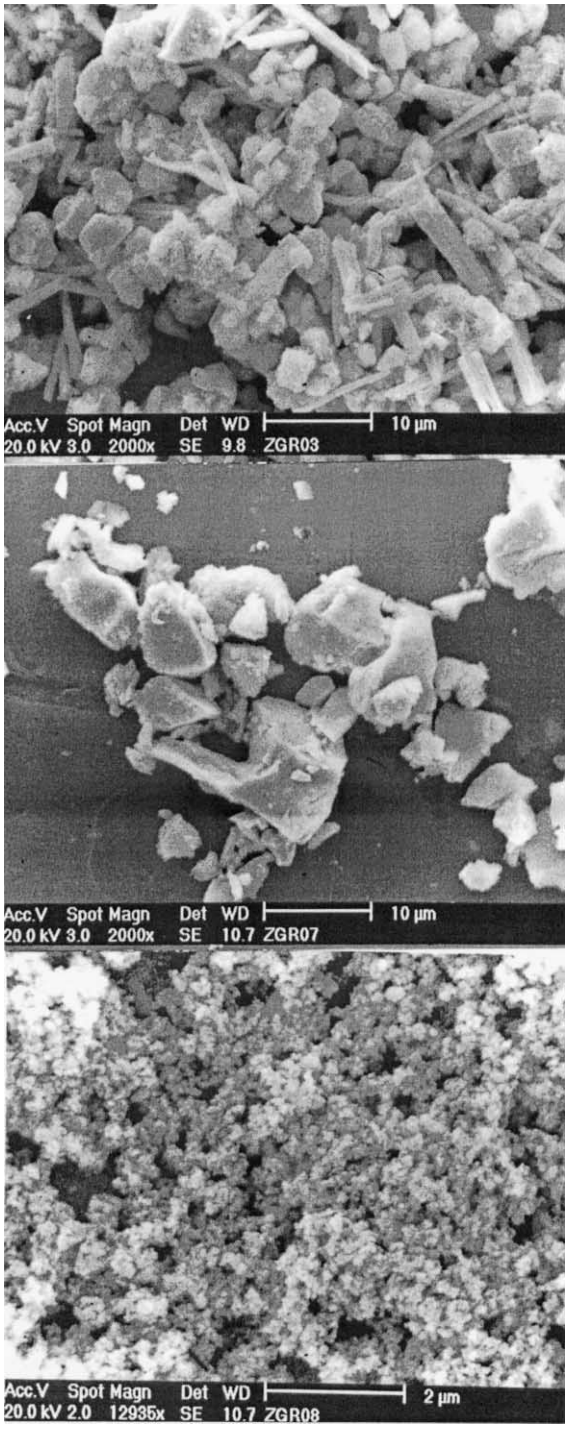

Fig. 3. Scanning electron microscopy micrographs of ZrO_2:Gd_2O_3 powders prepared by different chemical techniques. Top: citrate technique; middle: PVA technique; bottom: amorphous citrate technique.

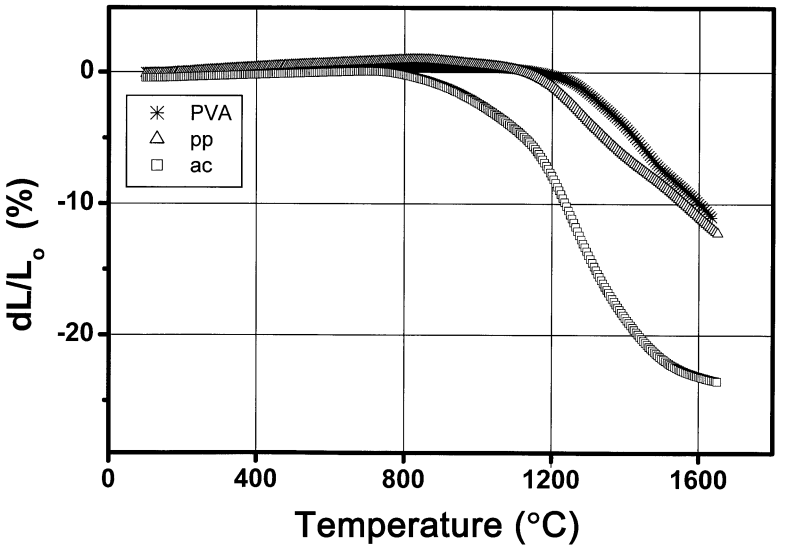

Fig. 4. Linear shrinkage curves of compacted ZrO_2:Gd_2O_3 powders prepared by different chemical techniques: citrate technique (pp); amorphous citrate technique (ac); PVA technique (PVA).

techniques is similar. The overall shrinkage up to 1600 °C is almost twice as large for the compact prepared by the amorphous citrate technique. Experimental efforts are now underway for the preparation by that technique of ZrO_2 using other rare earth dopants.

4. Conclusions

ZrO_2:Gd_2O_3 solid solutions prepared by similar techniques present significant thermal and microstructural differences. The PVA technique is found to be the easier route for solid solution synthesis. The highest degree of densification, on the other hand, was obtained for powders prepared by the amorphous citrate technique. The amorphous technique is then suggested here for the preparation of zirconia-based solid electrolytes having rare-earth ions as stabilizers.

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References

[1] E.C. Subbarao, in: A.H. Heuer, L.W. Hobbs (Eds.), Advances in Ceramics, V. 3, Science and Technology of Zirconia I, ACS, Columbus, OH, 1981, p. 1.
[2] D.W. Johnson Jr., Am. Ceram. Soc. Bull. 60 (1981) 221.
[3] D.W. Johnson Jr., in: G.L. Messing, K.S. Mazdiyasni, J.W. McCauley, R.A. Haber (Eds.), Advances in Ceramics, V. 21, Ceramic Powder Science, ACS, Westerville, OH, 1987, p. 3.
[4] M.P. Pechini, US Patent 3,330,697 (1967).
[5] M. Yashima, K. Ohtake, M. Kakihana, M. Yoshimura, J. Mater. Sci. Lett. 13 (1994) 1564.
[6] M. Yashima, K. Ohtake, M. Kakihana, M. Yoshimura, J. Am. Ceram. Soc. 77 (1994) 2773.
[7] R. Muccillo, N.H. Saito, E.N.S. Muccillo, Mater. Lett. 25 (1995) 165.
[8] O. Yokota, M. Yashima, M. Kakihana, A. Shimofuku, M. Yoshimura, J. Am. Ceram. Soc. 82 (1999) 1333.
[9] C. Marcilly, P. Courty, B. Delmon, J. Am. Ceram. Soc. 53 (1970) 56.
[10] M. Kakihana, S. Kato, M. Yashima, M. Yoshimura, J. Alloys Compd. 280 (1998) 125.
[11] S.K. Saha, A. Pathak, P. Pramanik, J. Mater. Sci. Lett. 14 (1995) 35.

[12] S.W. Kwon, S.B. Park, G. Seo, S.T. Hwang, J. Nucl. Mater. 257 (1998) 172.
[13] M.A. Gülgün, M.H. Nguyen, W.M. Kriven, J. Am. Ceram. Soc. 82 (1999) 556.
[14] S. Bhattacharyya, D.C. Agrawal, J. Mater. Sci. 30 (1995) 1495.
[15] R.J. Stafford, S.J. Rothman, J.L. Routbort, Solid State Ionics 37 (1989) 67.
[16] K.J. de Vries, T. van Dijk, A.J. Burggraaf, in: P. Vashishta, J.N. Shenoy, G.K. Shenoy (Eds.), Fast ion Transport in Solids. Electrodes and Electrolytes, North-Holland, Amsterdam, 1979, p. 679.