Materials Science Forum Vols. 299-300 (1999) pp 80-90

doi:10.4028/www.scientific.net/MSF.299-300.80

Synthesis of Reactive Ceramic Powders by the Citrate Technique

R. Muccillo[1], E.N.S. Muccillo[1], I.C. Cosentino[1], Y.V. França[1], F.C. Fonseca[1] and N.H. Saito[2]

[1] Instituto de Pesquisas Energéticas e Nucleares, Comissão Nacional de Energia Nuclear, C.P. 11049, Pinheiros, S. Paulo, S.P., 05422-970, Brazil

[2] Instituto de Pesquisas Tecnológicas do Estado de S. Paulo, Cidade Universitária, Butantã, 05508-901, S. Paulo, S.P., Brazil

Keywords: Powder Processing, Advanced Ceramics, Solid Electrolytes, Microstructure

Abstract The citrate technique has been used to produce homogeneous, fine and reactive ceramic powders. That technique consists basically in preparing polymeric resins by adding citric acid and polyethylene glycol to liquid solutions of the inorganic ceramic precursors, followed by controlled stirring and heating. High density bodies are then obtained after conformation and sintering the powders that resulted from the calcination of the resins. ZrO_2:MgO, ZrO_2:La_2O_3 and ThO_2:Y_2O_3 solid electrolytes to be used as electrochemical transducers in oxygen sensors, and Ag-$YBa_2Cu_3O_{7-x}$ composite high-T_c superconductors were obtained by that technique. The powders have been analyzed by sedimentation and gas adsorption techniques for determining particle size distribution, X-ray diffractometry for structural phase content, and Scanning and Transmission Electron Microscopy (SEM and TEM) for observation of particle agglomeration. The sintered solid electrolyte ceramic pellets, have been analyzed by XRD, by SEM for grain morphology, and Impedance Spectroscopy for bulk and grain boundary electrical characterization; the composite superconductor have been characterized by optical microscopy, XRD and four-probe electrical resistivity measurements.

Introduction

Ceramic oxide solid electrolytes are widely used as electrochemical transducers in oxygen sensors. The most common oxides that behave as oxygen-ion conducting solid electrolytes are ZrO_2:Y_2O_3, ZrO_2:CaO and ZrO_2:MgO [1]. The monitoring of oxygen dissolved in molten steels can be done with disposable oxygen sensors having ZrO_2:MgO solid electrolytes as electrochemical transducers [2,3]. The addition of about 3 wt% MgO in ZrO_2 followed by sintering at temperatures higher than 1400 °C produces partially stabilized zirconia (PSZ) with cubic/tetragonal and monoclinic phases. That level of stabilization was also found to give the highest value of dc ionic conductivity of ZrO_2:MgO solid electrolytes. Besides Y_2O_3 and MgO and CaO alkaline earth oxides, rare earth oxides are natural candidates for stabilizers of zirconia [4]. There are several ways of preparing ceramic solid electrolytes, namely, a) simply mixing the proper amounts of stabilizer to ZrO_2 , pressing and sintering at high temperatures and b) following one of a variety of chemical solution techniques. The advantages of the latter are that the powders exhibit improved chemical homogeneity and higher reactivity than the ones obtained by the conventional mixed oxide processes [5], enabling sintering to high densities at relatively lower temperatures. Amongst the solution techniques, the one that yields an amorphous organic resin that can be converted to homogeneous solid solution oxides upon heating is the citrate method [6]. In this paper, the synthesis of ZrO_2:MgO, ZrO_2:La_2O_3 and

ThO_2:Y_2O_3 solid electrolytes by the citrate method is described. Ag-$YBa_2Cu_3O_{7-x}$ high-T_c composite superconductors synthesis is also described as an additional example. The solid electrolyte powders, after characterization by X-ray diffractometry (XRD) for phase identification, sedigraph measurements for determination of agglomerate/particle distribution and Scanning Electron Microscopy (SEM) for particle size and morphology analysis, were pressed to pellets and sintered for microstructure characterization by SEM and XRD, and electrical characterization by impedance spectroscopy. The citrate route has been reported as a simple and efficient method for producing high quality $YBa_2Cu_3O_{7-\delta}$ (123) superconductor with better homogeneity and very fine grain size than by solid state reaction [7,8]. In this work the citrate technique for preparing $YBa_2Cu_3O_{7-\delta}$ -p wt% Ag superconductor composite (hereafter named 123-Ag) with $0 \leq p \leq 50$ (0 to 37.7 vol%) is described. Their characterizations by X-ray diffractometry, optical microscopy with polarized light and four-probe electrical measurements are also reported.

Materials and Methods

PROCESSING

Solid Electrolytes. The raw materials used were: > 99% pure hydrated zirconium oxide and thorium oxide produced at the Zirconium and Thorium Pilot Plants at IPEN-Brazil; BDH zirconyl chloride, 99.6% pure Sigma lanthanum oxide, concentrate Merck nitric acid, P. A. ethylene glycol, P. A. magnesium nitrate (99.5%). Yttrium oxide, of commercial origin, has been dissolved in thorium oxide following the citrate route. The experimental sequence for preparing ThO_2:Y_2O_3 is the following: citric acid and ethylene glycol (60:40 wt% ratio) are added to a mixture of thorium nitrate and yttrium nitrate for the desired stoichiometry of thoria-yttria solid electrolytes; the temperature bath, kept at 60 °C is raised to 110 °C for NO_2 elimination producing a brownish resin; the resin-to-oxide transformation is done in two steps: calcination at 400 °C/ 6 h in air yielding a black powder, followed by annealing at 800 °C/24 h under oxygen for carbon elimination and solid solution formation, yielding a light brown powder. Specimens with the same starting compositions as the ones prepared by the citrate method have been prepared by conventional solid state synthesis, namely, mixing, grinding, pressing and sintering. Similar procedure has been followed for processing ZrO_2: La_2O_3 and ZrO_2: MgO ceramic powders.

Composite Superconductors. The starting materials were $Y(NO_3)_3$ (78%), $Ba(NO_3)_2$ (P.A.), $Cu(NO_3)_2$ (P.A.) and $AgNO_3$ (P.A.). Yttrium, barium, copper and silver nitrates were dissolved in distilled water, added together in the desired stoichiometry and mixed under heating at 60 °C. Citric acid and ethylene glycol were then added for further heating in 100 °C-140 °C temperature baths. After approximately 5 hours a resin is obtained. Its calcination at 900 °C for 12 hours in oxygen at atmospheric pressure yields superconducting powders. The resulting powder was ground in an agate mortar and uniaxially pressed at 100 MPa into 12 mm diameter and 2 mm thickness pellets. Sintering has been achieved at 900 °C under oxygen.

CHARACTERIZATION

X-ray diffraction spectra of powders have been obtained at room temperature using a Philips diffractometer (PW3710) with Cu K_α radiation.

A model JXA 6400 JEOL scanning electron microscope was used to observe particle morphology and agglomeration state in ceramic ZrO_2: MgO powders. ThO_2: Y_2O_3 powder suspensions have been prepared for observations in a JEOL JEM200C Transmission Electron Microscope for the determination of average particle size and degree of particle agglomeration. Composite superconductor samples were polished with 15, 6, 3 and 1 μm diamond pastes for observation in an Olympus microscope (AHMT3) with reflected polarized light.

Electrical characterization of the solid electrolytes has been carried out by Electrochemical

Impedance Spectroscopy in the 5 Hz - 13 MHz frequency range from 250 °C to 600 °C with a 4192 A Hewlett Packard LF Impedance Analyzer connected via HPIB to a series 900 Hewlett Packard Controller. A sample chamber with three specimen holders made of inconel 600, alumina and platinum electrodes and leads has been built. The temperature of the specimens has been determined within 0.5 °C accuracy with a S-type Pt/Pt-Rh thermocouple with its sensing tip located close to the samples. Results on Impedance Spectroscopy of solid electrolytes have been published elsewhere [9-11].

Electrical measurements in the superconductors were carried out by the four-probe dc method with a Hewlett Packard 4328A milliohmeter. Specimen contacts were made with silver paint. Measurements were performed in the 77 K - 140 K temperature range with 1.5 mA injected current. The sample temperature was measured with a type T thermocouple attached to the specimen.

Results and Discussion

ZrO_2: MgO SOLID ELECTROLYTES

ZrO_2: MgO powders have been prepared following the experimental sequences of Fig. 1.

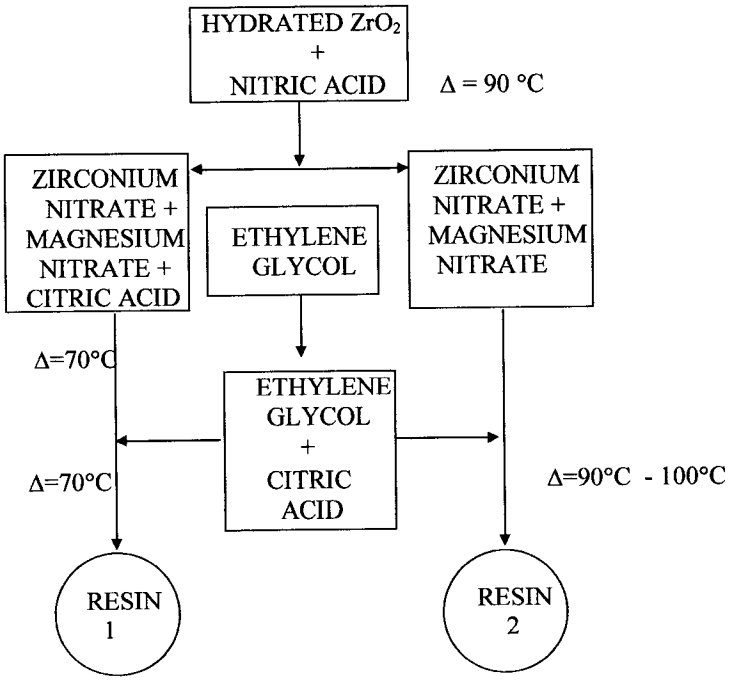

Fig. 1: Experimental sequences followed for the preparation of ZrO_2: MgO polymeric resins via the citrate method; Δ=bath temperatures.

After firing the resins resulting from sequences 1 and 2 at 450 °C, grinding and firing again at 800 °C, both powders (hereafter powders 1 and 2) had their average particle size determined by sedigraphic analysis; 1.1 μm and 4.0 μm are the values determined for powders 1 and 2, respectively. These powders are indeed agglomerated particles and the degree of agglomeration is found to be different for both powders, as shown in the SEM micrographs of Fig. 2.

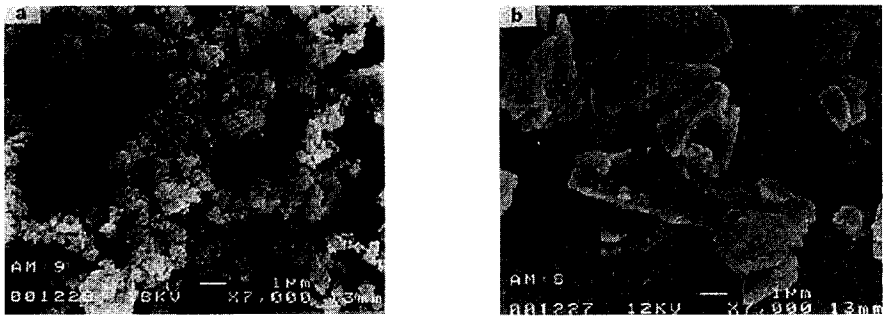

Fig. 2: Scanning electron micrographs of ZrO_2: 3.4 wt% MgO powders prepared by the citrate technique (a: route 1, b: route 2); bars = 1 μm.

The oxide powder processed according to sequence 1 exhibits a higher degree of agglomeration in comparison to that of sequence 2 (Cf. Figs. 2a and 2b). Powders obtained from sequence 1 consists of small spherical aggregates with few large particle agglomerates of irregular shapes. Powders from sequence 2 have aggregate particles with angular morphology with 2 to 6 μm average size.

In Fig. 3, X-ray diffractograms of ZrO_2: MgO powders obtained by the citrate technique are shown. Figs. 3A and 3B stand for partially (7.5 mol%) and fully (11.8 mol%) stabilized zirconia powders. Both spectra are similar and present only cubic diffraction lines.

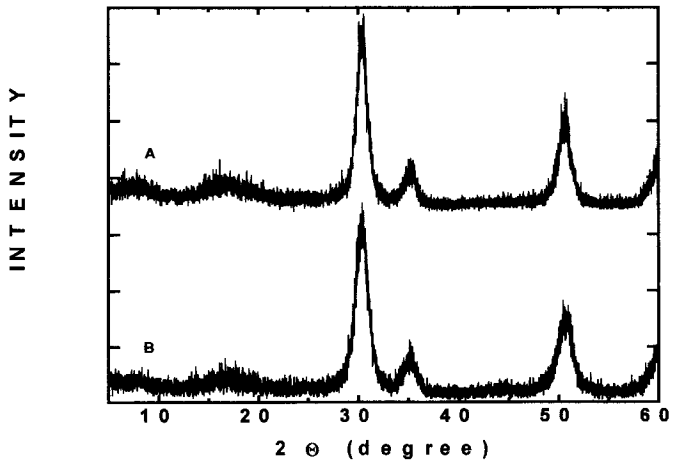

Fig. 3: X-ray diffraction patterns of partially (A: 7.5 mol%) and fully (B: 11.8 mol%) stabilized ZrO_2:MgO solid electrolytes prepared by the citrate technique.

ZrO_2: La_2O_3 SOLID ELECTROLYTES

Fig. 4 shows the experimental procedure used to obtain ZrO_2: La_2O_3 ceramic powders by the citrate technique. Calcination is carried out at 750 °C.

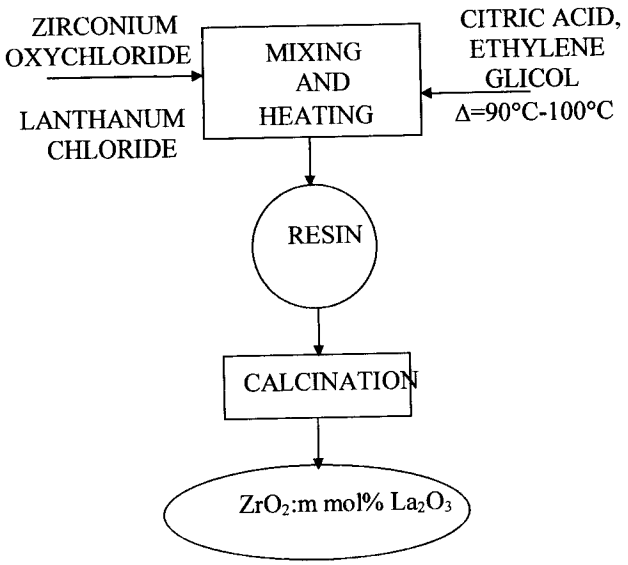

Fig. 4: Experimental sequences followed for the preparation of ZrO_2: La_2O_3 polymeric resins via the citrate method. Δ=bath temperatures.

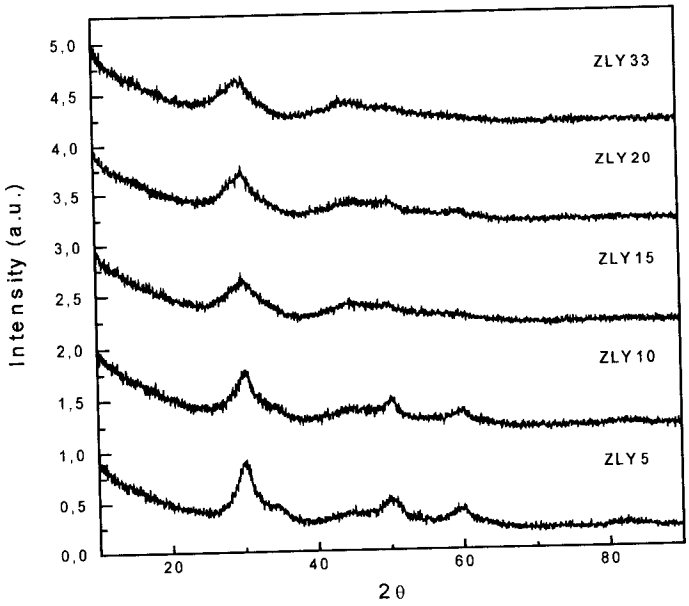

Fig. 5: X-ray diffraction patterns of ZrO_2: m mol% La_2O_3 powder, m=5, 10, 15, 20 and 33.

In Fig. 5, X-ray diffraction results of the ZrO_2: m mol% La_2O_3 powders obtained according to the sequence of Fig. 4 are shown for the 20° - 80° 2θ range, for m=5, 10, 15, 20 and 33. The main diffraction lines belong to the tetragonal phase, showing that stabilization of the zirconium oxide has been attained.

In Fig. 6 a SEM micrograph of a ZrO_2: La_2O_3 powder suspension is shown. It can be seen that powders with average particle size in the submicron range are obtained by the citrate technique.

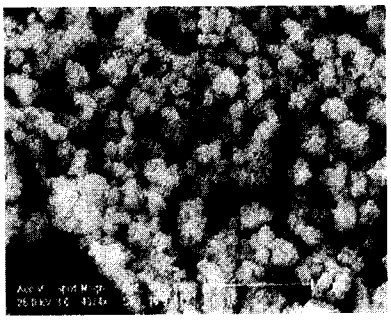

Fig. 6: Scanning electron microscopy micrograph of ZrO_2: 15 mol% La_2O_3 powders prepared by the citrate technique; bar = 1 μm.

ThO_2: Y_2O_3 SOLID ELECTROLYTES

Fig. 7 shows the experimental sequence for processing ThO_2: Y_2O_3 powders by the citrate technique.

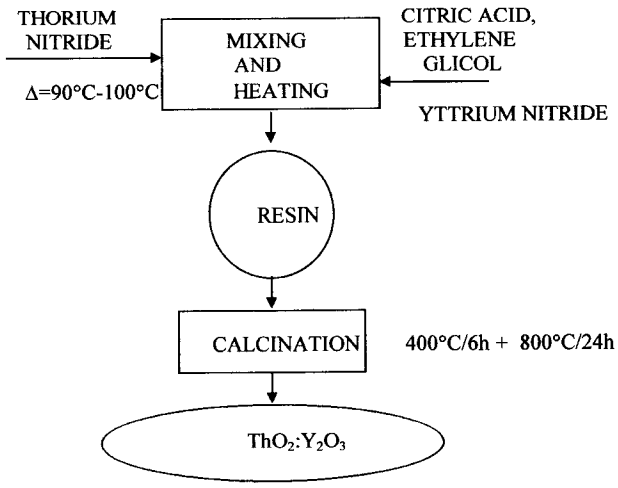

Fig. 7: Experimental sequences followed for the preparation of ThO_2: Y_2O_3 polymeric resins via the citrate method; Δ = bath temperatures.

Fig. 8 shows X-ray diffraction spectra of ThO_2: 9 mol% Y_2O_3 powders obtained by the citrate technique (Fig. 8a) and of pellets prepared from these powders and sintered at 1550 °C/2 h (Fig. 8b). The main diffraction lines of the thorium oxide fluorite phase are detected, from left to right: [100] 100%, [200] 35%, [220] 58%, [311] 64%, [222] 11%, [400] 8%, [331] 26% and [420] 17%, the numbers within brackets being the Miller indexes and the percentages the relative intensity, respectively.

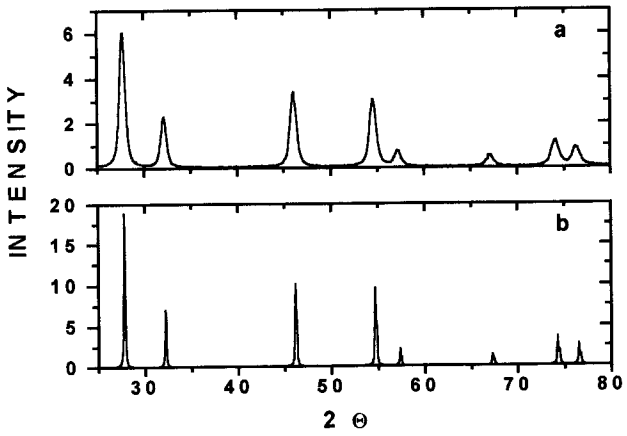

Fig. 8: X-ray diffraction patterns of ThO_2: 9 mol% Y_2O_3 powders obtained by the citrate method (a) and of pellets prepared from these powders and sintered at 1550 °C/ 2 h in air (b).

Fig. 9 shows a TEM micrograph of annealed ThO_2: 9 mol% Y_2O_3 powders. The powders are composed of a homogeneous distribution of particles with sizes as small as 30 nm. The main feature is that powders obtained by the citrate route are composed of very fine (in the nm range) particles. that explains the relative high densities reached after forming and sintering the ceramic pellets. In the same figure a SEM micrograph is shown for the sintered pellet prepared using these powders. A homogeneous microstructure with submicron average grain size is observed.

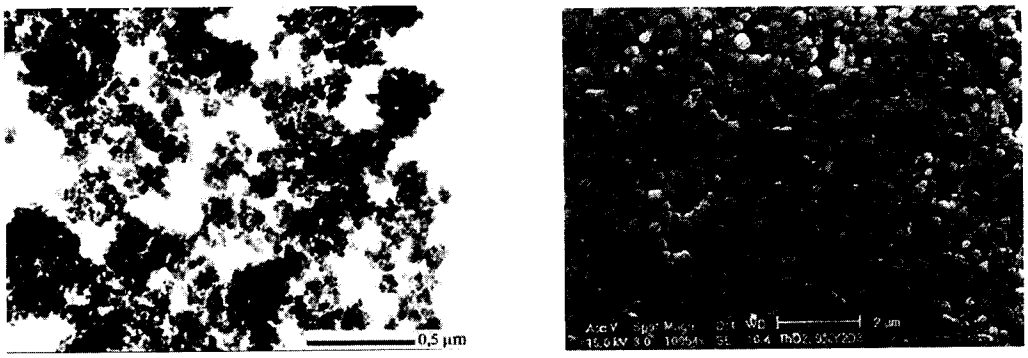

Fig. 9: TEM micrograph (left) of ThO_2: 9 mol% Y_2O_3 powder and SEM micrograph (right) of sintered pellet obtained by the citrate technique; bars = 0.5 µm (left) and 2 µm (right).

The impedance spectroscopy results of the zirconia- and thoria-based ceramic solid electrolytes, not depicted here, have shown that solid solution has been attained in all specimens prepared using powders processed by the citrate technique.

$YBa_2Cu_3O_{7-\delta}$-Ag COMPOSITE SUPERCONDUCTORS

Fig. 10 shows the experimental sequence followed for the preparation of $YBa_2Cu_3O_{7-\delta}$-Ag composites by the citrate method.

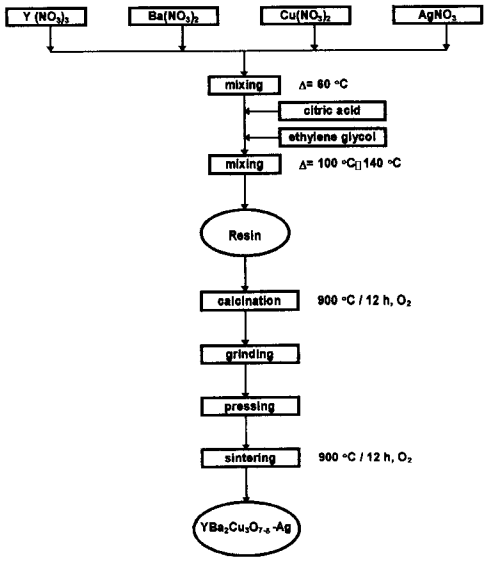

Fig. 10: Experimental sequence followed for preparing $YBa_2Cu_3O_{7-\delta}$-Ag composites by the citrate technique.

The X-ray diffractograms of $YBa_2Cu_3O_{7-\delta}$ powders without silver addition and with 3, 10 and 50 wt% (1.8, 6.3 and 37.7 vol%) silver are shown in Fig. 11, from top to bottom, respectively. All specimens show the diffraction lines corresponding to the orthorhombic superconducting phase. the diffraction lines belonging to specimens prepared with silver show the main diffraction lines of silver (2θ = 38.12/44.28/64.43/77.48 degrees).

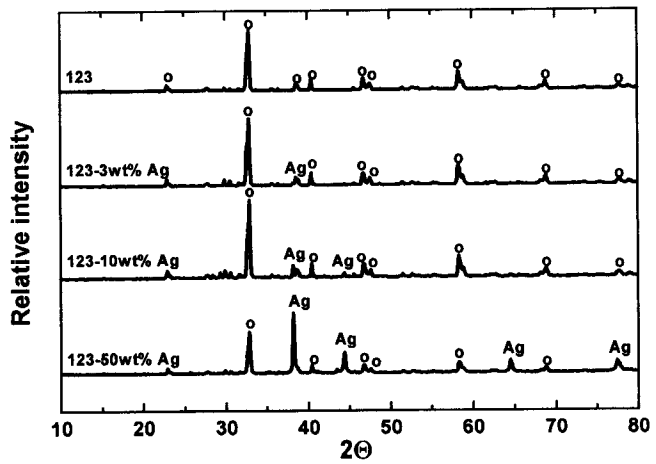

Fig. 11: XRD patterns of $YBa_2Cu_3O_{7-\delta}$-p wt% Ag for p=0 , 3 , 10 and 50; the main diffraction lines of the orthorhombic superconducting phase are marked as "o".

Fig. 12 shows optical micrographs of three composite superconducting samples: $YBa_2Cu_3O_{7-\delta}$ and $YBa_2Cu_3O_{7-\delta}$ with 0, 3 and 10 wt% Ag. A special feature is observed in the micrograph of the 3 wt% (1.8 vol%) Ag specimen: platelets (roughly 24 x 4 μm^2) are formed. Silver concentrations higher than the solubility limit of that element in 123 superconductors may cause the degradation of the platelet-like morphology. These platelets could act as paths for charge carriers in the superconducting state.

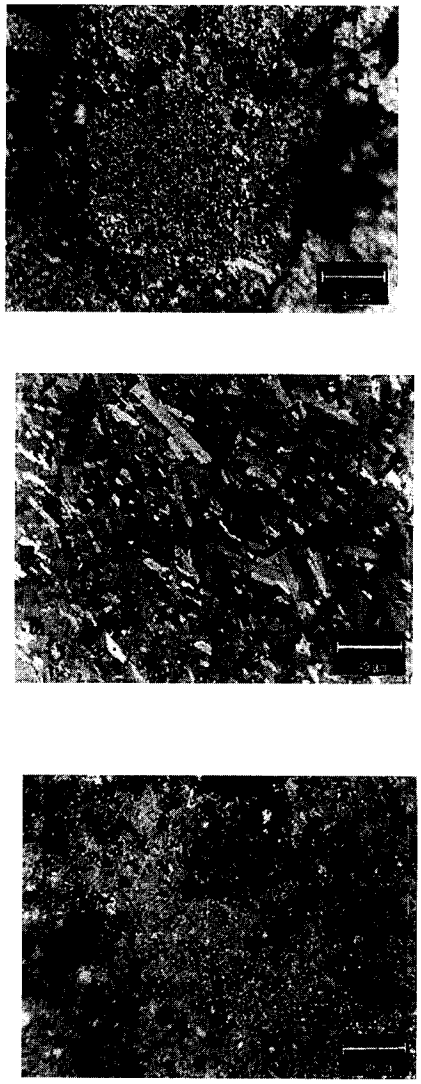

Fig. 12: Optical micrographs of $YBa_2Cu_3O_{7-\delta}$-p wt% Ag for p=0, 3 and 10; bars = 40 μm.

In Fig. 13 resistance measurements for four specimens are shown: 123-p wt% Ag for p=0, 3, 10 and 50.The resistance values have been normalized to the value measured at 140 K. Four sets of resistance values are shown. A full account of the electrical measurements in the composite superconductors can be found elsewhere [12,13].

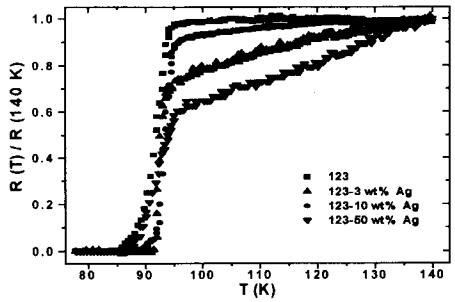

Fig. 13: Electrical resistivity curves for $YBa_2Cu_3O_{7-\delta}$-p wt% Ag composites for p=0, 3, 10 and 50.

Conclusions

Solid electrolytes of MgO-partially and fully stabilized zirconia with densities close to 100% of the theoretical density have been obtained after sintering pellets prepared from powders produced by the citrate technique. ZrO_2: La_2O_3 reactive powders have also been processed by the citrate technique.

Reactive thoria-yttria powders have been obtained by the citrate technique. Pellets made using these powders reached higher than 90% of the theoretical density after sintering at 1550 °C, a temperature lower than 50% of the melting point of thorium oxide.

The citrate technique can then be used to produce powders to manufacture zirconia- and thoria-based solid electrolytes to be used as electrochemical transducers in oxygen sensing devices.

$YBa_2Cu_3O_{7-\delta}$-Ag superconducting reactive powders have been prepared by the citrate technique, allowing for the preparation of dense superconductors with sharp temperature transition between the normal and the superconductor states.

Final conclusion: The citrate technique is a powerful technique for processing reactive solid electrolyte and high -T_c superconducting ceramic powders for use in advanced ceramics technology.

Acknowledgments

To Celso V. de Morais, Nildemar A. M. Ferreira, Donis Perini, Dr. K. F. Portella and Dr. A. H. A. Bressiani. To CNEN, FAPESP and PADCT-TR for financial support. To FAPESP for scholarship to F. C. Fonseca and CNPq to I. C. Cosentino, N. H. Saito and R. Muccillo.

References

[1] R. M. Dell, A. Hooper, In: *Solid Electrolytes - General Principles, Characterization, Materials, Applications*, ed. P. Hagenmuller, W. Van Gool. Academic Press, New York, 1978, p. 291.
[2] R. Stephen, Stahl u. Eisen **94** (1974) p.547.
[3] K. Yamada, Y. Shinya, K. Tanaka, Solid State Ionics **3/4** (1981) p. 595.
[4] W. Pyda, K. Haberko, Z. Zurek, J. Eur. Ceram. Soc. **10** (1992) p. 453.
[5] H. U. Anderson, C. C. Chen, J. C. Wang, M. J. Penneli, In: *Ceramic Powder Science III* (Ceram. Trans. **12**), ed. G. L. Messing, S. Hirano, H. Hausner, The Am. Ceram. Soc., Westerville, OH, 1990, p. 749.
[6] M. Pechini, US Patent No. 3,330,697, July 11, 1967.
[7] P. Karen, A. Kjekshus, J. Am. Ceram. Soc. **77** (1994) p. 547.

[8] G. Szabo-Miszenti, L. Gherardi, P. Caracino, P. Metra, In: *Applied Superconductivity* v. 2, ed. H. C. Freyhardt, 1993, p. 1609.
[9] R. Muccillo, N. H. Saito, E. N. S. Muccillo, Mat. Lett. **25** (1995) p. 165.
[10] I. C. Cosentino, R. Muccillo, Mat. Lett. **32** (1997) p. 295.
[11] R. Muccillo, I. C. Cosentino, D. Z. De Florio, Y. V. França, XII Brazilian Congress on Engineering and Science of Materials, Águas de Lindóia, S. P., Brazil, 1996, p. 113.
[12] F. C. Fonseca, M. Sc. Dissertation (in Portuguese) IPEN-USP, 1996.
[13] F. C. Fonseca, R. Muccillo, Physica C-Superconductivity **267** (1996) p. 87.

R. Muccillo e-mail: muccillo@usp.br

Advanced Powder Technology I
doi:10.4028/www.scientific.net/MSF.299-300

Synthesis of Reactive Ceramic Powders by the Citrate Technique
doi:10.4028/www.scientific.net/MSF.299-300.80