Mat. Res. Bull., Vol. 24, pp. 1119-1126, 1989. Printed in the USA.
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THE POLYACRYLAMIDE GEL: A NOVEL ROUTE TO CERAMIC AND GLASSY OXIDE POWDERS

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(Received June 19, 1989; Refereed)

ABSTRACT

A process for elaborating mineral oxide powders is described. An aqueous solution is first made containing the cations complexed by citric acid. This aqueous solution is gelled by an organic polymer network: the polyacrylamide. The gel is calcined in an aerated furnace to the desired temperature. This process is valuable for a great number of compounds, is of great simplicity and provides ultrafine powders at relatively low temperatures. It is illustrated by three examples: $YBa_2Cu_3O_{7-x}$, $2SiO_2$-$3Al_2O_3$ (mullite) and $LaAlO_3$ powders.

MATERIALS INDEX: **polyacrylamides, gels, oxides, powders**

Introduction

Although the most common method for ceramic powder elaboration, i.e: grinding of mixed oxide powders followed by solid state reactions, is adaptable to a large scale production, it presents several drawbacks such as high reaction temperatures, large particle sizes, limited degree of chemical homogeneity, possible introduction of impurities from grinding, large porosities and low sintering ability. For several years, numerous "chemical" processes have been studied and developed for elaborating at lower temperatures finer and more homogeneous powders.

In the case of mixed oxides, the chemical homogeneity is reached at a molecular level in gaseous or liquid solution precursors. The most sophisticated routes developed for trying to preserve this chemical homogeneity till the obtention of the oxide powders are sol-gel (hydrolysis, condensation and polymerization of metal alkoxides in organic medium or of metal salts in aqueous solution), salts or hydroxides coprecipitation, citrate calcination, spray drying, spray pyrolysis, lyophilization, microemulsions, hydrothermal processes...(1).

Among them, the sol-gel (2) is very attractive. Up to now, in this process, the gel is built up by chemical or physical bonds between the mineral species. The purpose of this communication is to describe a new process for the preparation of mineral powders by a "solution-gel-calcination" route, where the gel network is made by an organic polymer independant of the mineral species in solution.

Description of the Process

Starting from an aqueous solution containing all the required elements in the appropriate ratios the process consists in the gelation of the solution by an organic polymer, followed by the calcination of the as obtained gel.

Aqueous Solution

An aqueous solution, or a stable homogeneous sol mixture, containing all the desired elements in their stoichiometric ratios is required. The stability of the solution against hydrolysis or condensation may be easily improved by complexing the cations by a chelating agent, such as citric acid, generally with one citric acid per valence of each metal. If needed, the excess of acidity of the citric acid is neutralized by ammonia. The elements are supplied from the commercial chemicals: oxides, hydroxides, alkoxides, and salts like nitrates, carbonates, acetates... . Anions able to make stable and not desired compounds after the calcination step (ex: sulphates in the presence of barium) have to be avoided.

Gelation

The gelation of the solution is achieved by in situ creating an organic polymeric network, which is a priori chemically independant of the other species previously in solution. The simplest and easiest irreversible hydrophilic polymeric network is the polyacrylamide gel (3). The monomers, acrylamide and N,N'-methylene-bis-acrylamide, are easily dissolved in water. The polymerization is initiated by free radicals afforded by persulphates, peroxides, azobisisobutyronitrile (AIBN)..., and is promoted by radical transfer agents like N,N,N',N'-tetramethyl-ethylenediamine (TEMED) (4). By heating the solution, a transparent gel is rapidly obtained. The gel, a diphasic medium, is therefore constituted by the polyacrylamide polymer network "immobilizing" the precursor solution of the inorganic oxides, glasses or ceramics.

Calcination

The gels are transferred in crucibles (alumina, silica, porcelain,...), put in a ventilated furnace and raised to a temperature such as practically all the water and the organic species are removed. At the end of this step it remains a heap of fine and light oxide powder.

Experimental Examples

This new process for elaborating ceramic or glassy powders is illustrated by three practical examples.

Preparation of Fine Powder of the $YBa_2Cu_3O_{7-x}$ Superconductor Oxide

6.45 g (0.0285 mol) of yttrium oxide Y_2O_3 are first dissolved in concentrated nitric acid in light excess. This nitrate is added to 0.7 L of aqueous solution containing 156 g (0.743 mol) of citric acid monohydrate $C_6H_8O_7.H_2O$; 22.54 g (0.114 mol) of barium carbonate $BaCO_3$ and 34.216 g (0.171

mol) of copper acetate monohydrate $Cu(C_2H_3O_2)_2.H_2O$ are then dissolved in the solution. The pH is raised to 7 by addition of ammonia and distilled water is added to have 1 L of solution. So a blue and very stable $YBa_2Cu_3O_{7-x}$ precursor solution is obtained, at 0.057 $mol.L^{-1}$ concentration.

In 0.4 L of this solution are dissolved 24 g of acrylamide, 2.4 g of N,N'-methylene-bis-acrylamide, 0.4 mL of TEMED and 4 mL of a 3% hydrogen peroxide solution. The solution is divided in three parts and gelled in a water bath at 80°C in 15-20 minutes. The three blue transparent gels are transferred in a wide porcelain cap and put in a programmable and aerated furnace. The temperature of the furnace is raised to 800°C at the rate of 1.2°C mn^{-1} and maintained at 800°C for 5 hours.

Preparation of Mullite Precursor Powder

A "SiO_2 precursor solution" is obtained by pouring 28.7 g (0.138 mol) of tetraethylorthosilicate $Si(OC_2H_5)_4$ in about 1 L of an aqueous solution containing 35 g (0.167 mol) of citric acid monohydrate $C_6H_8O_7.H_2O$. The mixture is let under stirring for a night. A clear solution is obtained containing 7.6 10^{-3} g of "SiO_2" per g of solution. This solution is stable for several weeks. By the same manner, 61.94 g (0.303 mol) of aluminum isopropoxide $Al(OC_3H_7)_3$ are dissolved in 0.6 L of an aqueous solution containing 200 g (0.95 mol) of citric acid monohydrate. A clear and stable solution is obtained, containing 2.13 10^{-2} g of "Al_2O_3" per g of solution.

Starting from 124 g of the "Al_2O_3 solution" and 136.4 g of the "SiO_2 solution", a mixture of $2SiO_2$-$3Al_2O_3$ composition is realized. This solution is perfectly clear; 15 g of acrylamide, 1.25 g of N,N'-methylene-bis-acrylamide, 0.25 mL of TEMED and 5 mg of ammonium persulphate $(NH_4)_2S_2O_8$ are dissolved in this solution. The mixture is divided in two batches and heated at 80°C, the gelation occurs in less than half an hour.

The gels are transferred in alumina crucibles and put in a programmable and aerated furnace. Its temperature is raised to 800°C at the rate of 1.2°C mn^{-1} and maintained at 800°C for 4 hours.

Preparation of $LaAlO_3$ Powder

An equimolar solution of lanthanum and aluminum nitrates is realized by dissolving 0.055 mole of each individual nitrate in 1 L of aqueous solution. Three gels are made from three samples of 100 mL of this solution. In the sample A, 4 g of acrylamide and 0.2 g of N,N'-methylene-bis-acrylamide are dissolved; in the sample B, 20 g of acrylamide and 8 g of N,N'-methylene-bis-acrylamide; and in the sample C, three equivalents of citric acid per each cation and ammonia to raise the pH to 8 are added, and then 6 g of acrylamide and 0.5 g of N,N'-methylene-bis acrylamide. The solutions are heated to about 90°C while 0.1 mL of TEMED and 50 mg of AIBN dissolved in 2 mL of ethanol are added. In the three cases, gels are obtained within a few minutes: two gels of nitrates (A: weakly reticulated and B: hardly reticulated) and one gel of citrate (C). The three gels are pyrolyzed at 2°C mn^{-1} up to 850°C and maintained at this temperature for 5 hours.

Results and Discussion

The three examples of $YBa_2Cu_3O_{7-x}$, mullite and $LaAlO_3$, presented and discussed here, have been chosen through a great number of complex oxide powders of different natures and compositions elaborated by this process.

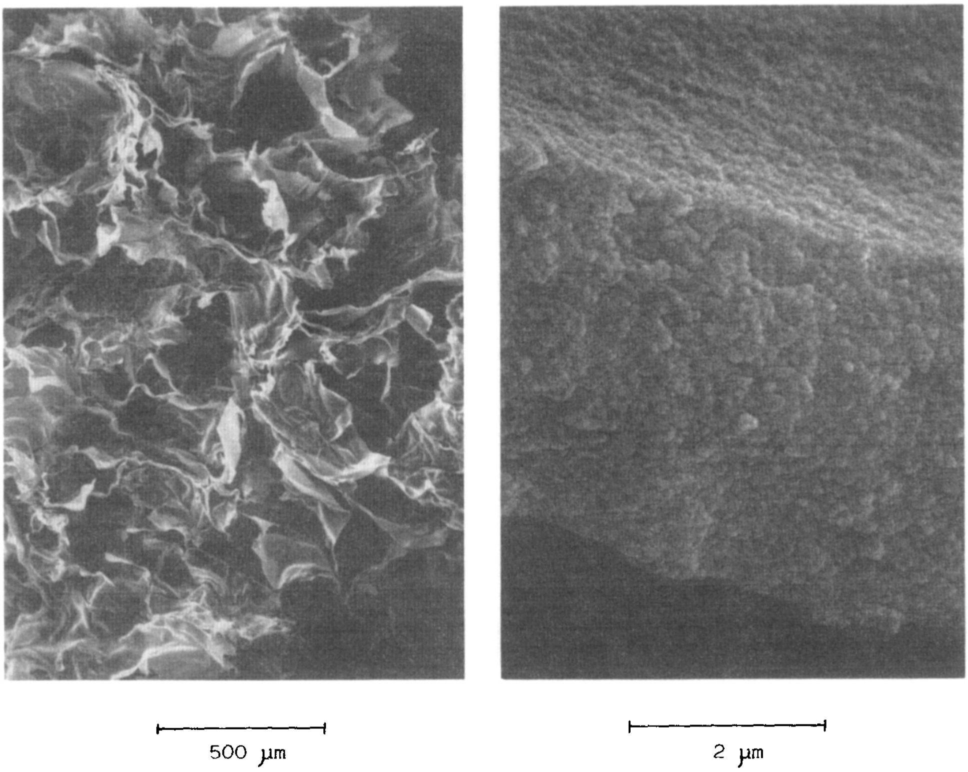

FIG.1
SEM microstructures of the mullite precursor powder obtained at 800°C.

$YBa_2Cu_3O_{7-x}$ Powder

At 800°C, 15 g of a black and very aerated powder are obtained, in three heaps having roughly the same shape than the three gels before calcination.

At this stage the chemical reaction is almost finished; the X-ray diffraction pattern reveals only small traces of barium carbonate in addition to the $YBa_2Cu_3O_{7-x}$ phase. This phase is tetragonal and remains tetragonal (with disappearence of the carbonate traces) even after longer annealing times at 800°C and slow cooling to room temperature. This has been observed by other authors for powders obtained at relatively low temperatures, as for instance from oxalates (5,6). It may be due to an incomplete crystallization. After annealing at 860°C in air for a few hours followed by a slow cooling, the powder was transformed to its orthorhombic form. The samples, pressed into pellets and sintered at 950°C in oxygen and slowly cooled, exhibit good superconducting properties with a T_c at 93 K (7).

Several authors (8-11) have prepared $YBa_2Cu_3O_{7-x}$ by the amorphous citrate route (12). This method is reported to give highly reactive and homogeneous powders. However problems may arise when concentrating nitrates in the presence of organic materials. A violent reaction of decomposition of the organic part could occur (13). It often results in hard agglomerates due to an uncontrolled temperature. This problem is avoided in the polyacrylamide gel process since there is no concentration step. The $YBa_2Cu_3O_{7-x}$ powders elaborated by this process are more light and aerated, constituted of submicronic particles (0.1-0.2 µm) weakly agglomerated in sheets, the specific surface being typically 5-6 m^2g^{-1}. The great advantage of this process over other methods is its great simplicity. Numerous compositions have been made so far to investigate the phase diagram of the system Y_2O_3-BaO-CuO (14).

Fine and homogeneous Bi-Pb-Sr-Ca-Cu-O superconductor oxide powders have been also easily obtained from the corresponding stable aqueous solutions (pH 7).

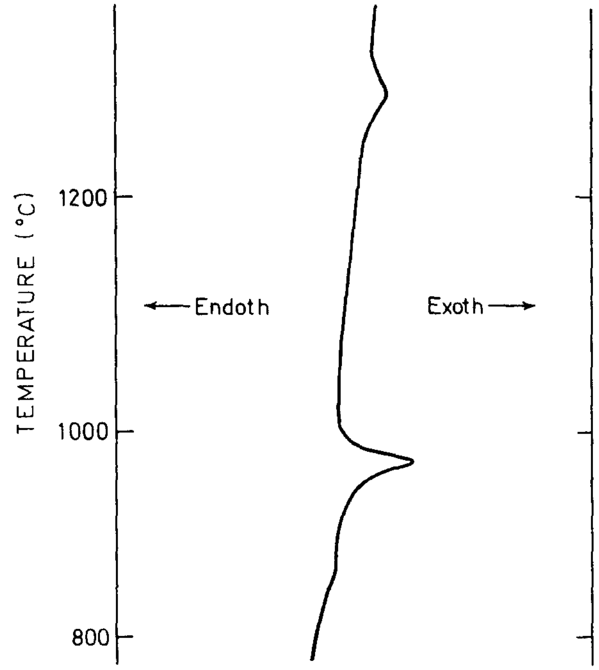

FIG.2
DTA curve of the mullite precursor powder between 800 and 1300°C heating rate: 10°C mn^{-1}.

Mullite Powder

At 800°C, two heaps of white powder are obtained having roughly the aspect of cauliflowers. The Fig.1 represents two microstructures by scanning electron microscope (SEM) of this powder. It is constitued of thin sheets; the agglomerate size is estimated to be roughly 0.1 µm. A specific area of 210 m^2g^{-1} has been measured by nitrogen adsorption (BET). The differential thermal analysis (DTA) from 800 to 1300°C (Fig.2) reveals an exothermic peak at about 970°C and another one beginning at 1250°C. For following the crystallization, the powder has been annealed at different temperatures for periods of 15 hours (at 930, 1030, 1100, 1150 and 1200°C). From 800 to 1100°C we observe by X-ray diffraction only broad and faint peaks of a structure attributed to a spinel phase (15-17); at 1150°C the peaks of the mullite phase $2SiO_2$-$3Al_2O_3$ begin to appear and at 1200°C there is only the pure mullite phase more crystallized. There is therefore no crystallization of the "primary mullite" (18) or "cubic mullite" (19) at about 970°C but a slow crystallization of the "secondary, ordinary or orthorhombic mullite" is observed at higher temperatures. Further studies are necessary to understand the controversial nature of the exothermic peak at 970°C and compare the mullite obtained by this process to the materials elaborated by other processes.

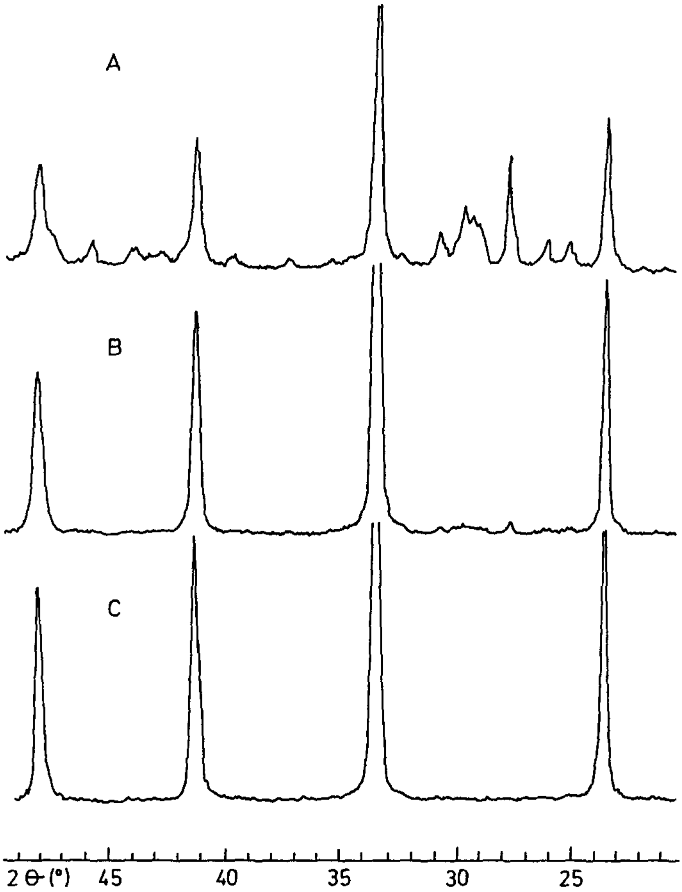

FIG.3
XRD spectra (Cu Kα) of $LaAlO_3$ powders obtained at 850°C from A: nitrates solution, weakly reticulated gel; B: nitrates solution,strongly reticulated gel; and C: citrates solution, "normal" gel (see text).

The amorphous citrate process has been used chiefly for mixed oxides with transition metals. We have shown the possibility to extend this route by using the citrate polyacrylamide gel process for the elaboration of silicate and aluminosilicate powders. The mullite composition is one example. There is no problem for preparing clear aqueous precursor solutions containing silicon, although there is probably no complex formation between citric acid and silicon in these conditions. These solutions are stable in acidic medium for weeks. Recently, silica hydrosols have been produced without addition of alcohols in aqueous sol-gel processes (20,21). Homogeneous sols mixtures may also be easily gelled by a polyacrylamide network.

$LaAlO_3$ Powder

The third example has been chosen for trying to show the respective contributions of the complexation of the cations by the α-hydroxy acid function of the citric acid and of the polyacrylamide gel on the chemical homogeneity of the powders. On the Fig.3 are reported the XRD spectra of the three powders obtained at 850°C. For the powder C, i.e. citrates, there are only the peaks of the pure rhombohedric structure of $LaAlO_3$. On the spectrum of the powder A, i.e. nitrates, weakly reticulated gel, there are many secondary phases and much less for the powder B, i.e. nitrates, hardly reticulated gel. Thus one can see that in the same thermal conditions, the powder from a citrate solution (C) is more chemically homogeneous than from nitrate solutions (A and B). For nitrate solutions the more reticulated the polyacrylamide gel (B) is, the more chemically homogeneous is the powder.

Conclusion

This new process for elaborating ultrafine oxide powders precursors of glasses or ceramics is very general and seems to be valuable for a great number of desired compositions. It is easy to work and is not time consuming. It suffices to have a stable aqueous solution or a stable colloidal mixture. The aqueous solutions may be easily achieved from the most common chemicals: nitrates, carbonates, acetates, oxides, hydroxides, alkoxides,... . The mixture may be gelled at acid, neutral, or even basic pH. One may vary the concentration and the pH of the solution and the reticulation of the polyacrylamide gel. This process provides ultrafine powders at relatively low temperatures and metastable phases or even glasses can be obtained.

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