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Exploring the polyvinyl alcohol method for preparing cuprates and manganites

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Abstract

The polyvinyl alcohol route is investigated in the formation of cuprate and manganite ceramics. By evaporation of the nitrate solution containing the stoichiometric quantities of the cations and the PVA, a spongy mass is produced, which upon a single calcination converts into the desired phases. We chose $YBa_2Cu_3O_y$, a high temperature superconductor, and $La_{2/3}Ca_{1/3}MnO_3$, a perovskite manganite showing colossal magnetoresistance as case studies for the preparation of technological interesting ceramic powders. XRD is employed to monitor the phase transformation leading to the single phases. Moreover, carbon content in the final powders is measured to assure complete elimination of carbonaceous species. This preliminar study shows that the PVA solution can be a potentially interesting technique to prepare these advanced ceramic powders as compared to classical ceramic methods.

Keywords: Calcination; (La,Ca) MnO_3; Oxide superconductors; Polyvinyl alcohol; Powders: chemical preparation; Transition metal oxides; YBCO

1. Introduction

Wet chemistry methods often lead to more homogeneous, fine and fast ceramic powders as compared to the classical solid state technique of repetitive calcining and homogenising steps. Among them, the sol-gel technique is being extensively investigated for the preparation of a large number of advanced ceramic powders starting from different precursors, solvents, gelation and drying steps. This involves the formation of a polymeric inorganic network by hydrolysis–condensation reactions with water as the usual solvent. From an industrial point of view, sol-gel techniques are seen as complex processes involving several steps such as precursor preparation, mixing, gelation, aging, drying and calcination. In addition, handling of highly toxic metalorganic species in sol-gel technology is avoided in the PVA method, being possible to use rather simple salt derivatives like nitrates. However, thermal polymer degradation can also lead to volatile toxic compounds although to a lesser extent than in sol-gel processing, in which large amounts of organics are usual. As a consequence, it would be desirable to obtain the powders by means of a process involving few operations yet retaining the potential of sol-gel techniques, specially those aspects concerning initial precursor reactivity.

Some authors have already explored the PVA route for preparing some specific ceramic materials: concrete powders,[1] fuel cell cathodes[2] or cordierite.[3]

The method consists of starting from an aqueous solution of soluble salts, usually nitrates, and adding some amount of polyvinyl alcohol (PVA). PVA, CH_3–$(CH_2$–$CHOH)_n$–CH_2OH is a polyhydroxylated polymer, miscible with water in all proportions, which can be decomposed thermally at temperatures below 600 °C. As water evaporates, the solution becomes progressively thickened. In the end, gelation occurs by entanglement of the long PVA chains, which derives in a disordered network able to entrap the precipitated cationic compounds inside. Depending on the cation chemistry, some hydrolysis in this step may be produced, in a similar fashion to Fe_3O_4 precipitation in the presence of PVA as reported by Lee et al.[4] Simultaneously, bubbles originating from solvent evaporation and decomposition products such as nitrogen oxides develop in the viscous solution, eventually leading to a foam-like

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structure. Calcination of these foams renders the desired phase by the correct thermal treatment.

In this work, we are focusing more on electronic advanced ceramic materials. In particular, some aspects on segregation during gelation have been pointed out to be a major concern, for instance, the precipitation of low-solubility salts during solvent evaporation.[5] For instance, this happens with barium nitrate (90 g/l solubility in boiling water) in Ba-containing substances.

As case studies, a high critical temperature superconductor cuprate containing barium ($YBa_2Cu_3O_{7-\delta}$) and a colossal magnetoresistive perovskite manganite ($La_{2/3}Ca_{1/3}MnO_3$) are synthesised by the PVA method at a laboratory scale.

2. Experimental

Stoichiometric quantities of Y_2O_3 99.9% (Aldrich), $BaCO_3$ 99.99% (DIOPMA), CuO 99.99% (DIOPMA), La_2O_3 99.9% (Aldrich), $CaCO_3$ 99.99% (DIOPMA) and MnO_2 99.9% (DIOPMA) powders were weighed and dissolved simultaneously in hot concentrated nitric acid, 10 g of each compound were synthesized.

PVA with a polymeration degree of 630 (FLUKA) was predissolved in a certain amount of water under vigorous stirring in a glass beaker. Then, it was slowly added to the cation solution in order to avoid excessive foaming. By means of a hot plate, evaporation proceeded with simultaneous thickening of the solution. In the last step, bubbles get trapped in the gel, which collapses with heating into a black, crispy powder.

The weight ratio of oxide powders to PVA was 5:1. This proportion allows a viscous solution to be formed and the absence of flames during gel drying in the hot plate. The initial PVA concentration in the cation solution was 0.01 g/ml.

These calcined foams are heated in a muffle furnace in high-grade alumina crucibles in air to obtain the desired phases in a single thermal treatment.

Powder XRD diffraction (CuK_α radiation) was performed in a SIEMENS D-5000 model apparatus. Lattice parameters were refined by the least squares method with CELREF version 3 program.

Carbon and nitrogen impurities expressed as C and N ppm respectively are analysed with a chromatographic technique using an ANALYTICAL PRECISION instrument model EA1108 with helium as the carrier gas.

DTA and TGA heating curves were recorded in independent home-made devices connected to a PC computer. The heating rates were 1 and 5 °C/min, respectively.

3. Results and discussion

3.1. $YBa_2Cu_3O_{7-\delta}$

This is an interesting case because of the presence of a Ba-rich phase such as the Y-123. After the acid dissolution, no precipitated white $Ba(NO_3)_2$ particles could be observed in the blue solution since the mixture was unsaturated. Then predissolved PVA solution is added, making the solution colour turn from blue to green. This is thought to be a consequence of Cu^{2+} complex

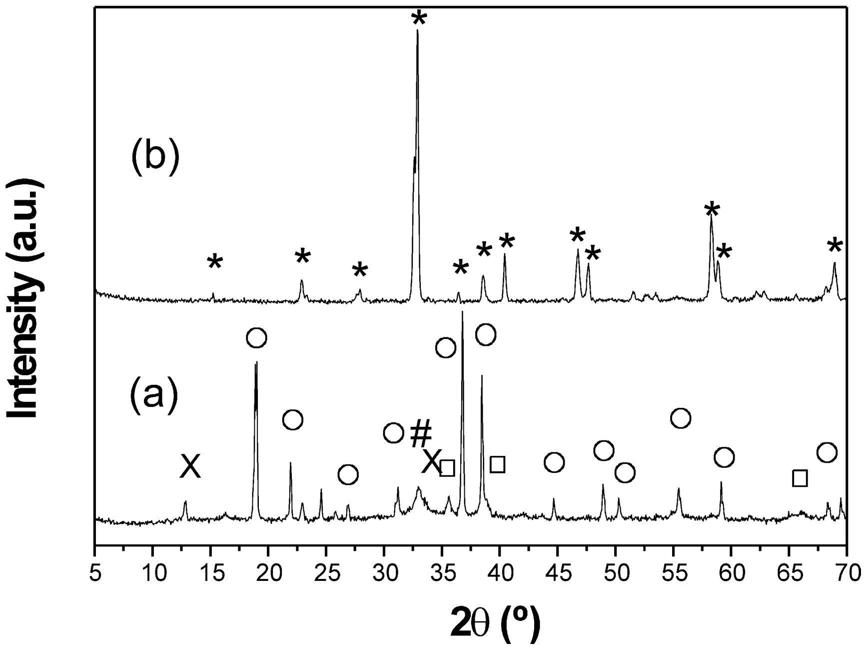

Fig. 1. Powder X-ray diffraction pattern corresponding to the Y-123 PVA precursor crusts (a) and calcined powder at 900 °C/24 h (b). Symbols stand for: "○" $Ba(NO_3)_2$, "□" CuO, "X" $Cu_2(OH)_3NO_3$, "*" Y-123 and "#" $Y_2Cu_2O_5$.

formation with the hydroxyl groups in the PVA chains. Solvent evaporation produces partial barium nitrate precipitation as it becomes progressively saturated. The viscosity of the solution increases as water is eliminated with simultaneous evolving of NO_x gases until a greenish foam forms which then transforms to a black crust.

XRD patterns of the calcined ashes (Fig. 1a) shows predominantly $Ba(NO_3)_2$ together with CuO, $Cu_2(OH)_3NO_3$ and possibly $Y_2Cu_2O_5$ intermediate phase.

Calcined products are displayed in Fig. 1b at 950 °C/1 h in air. Only reflection peaks assigned to Y-123 are observed. No $BaCO_3$ characteristic doublet peak is observable at 24°, indicating that $BaCO_3$ has decomposed within XRD detection limits. This data demonstrates the full completion of the reaction leading to Y-123 by the PVA method although some barium nitrate segregation occurs. It is thought that fine barium nitrate grains distribute uniformly in the foamy gel resulting in short diffusion paths and enhanced reactivity.

Thermogravimetric analysis was performed with the obtained Y-123 crusts (Fig. 2). A 10% weight loss up 140 °C is assigned to water evaporation. Main weight loss occurs at 300 °C, which seems to consist of two different events, in a similar fashion to the work of Morell et al.[6]

A clearer picture is obtained with the DTA measurement, shown in Fig. 3. Thermal events under 400 °C are assigned to PVA combustion/decomposition, according to a two-step mechanism. Pure PVA dehydration is reported to be in the 250–400 °C interval leading to a polymer-type structure followed by a de-polymerisation between 400 and 600 °C giving formaldehyde, acroleine and acetaldehyde.[7] Interestingly, there is a reduced decomposition temperature compared to pure PVA. In our case, the exothermic signal occurs at 150 °C. Although this temperature varies slighly with polymer molecular weight,[6] a remarkable 100 °C decrease is observed in our case. This reduction might be a consequence of oxidising action of nitrates on the PVA and the presence of copper(II) ion which is known to strongly catalyse the polymers degradation.[8]

As for elemental analysis, nitrogen measurements give a track of nitrate decomposition of the cationic salts. In the calcined xerogel this value was 72,100 ppm (7.21% N). This indicates that some amount of nitrate salts still exist in the precursor crusts as confirmed also by XRD data, mainly in the form of barium nitrate. As expected, no sign of nitrogen is observed in the calcined powders.

In addition, carbon content of this powder gives 3600 ppm C. Carbon impurities in superconductor Y-123 are specially detrimental to its superconducting properties owing to T_c depression leading to low critical currents.[9]

In order to diminish this value, two different thermal treatments were attempted: 970 °C for 5 h and a longer treatment at 900 °C for 24 h, both in air. Results are summarised in Fig. 4. It is observed that more effective carbon elimination is achieved when longer treatments at lower temperatures are chosen. In fact, 550 ppm are reached in the longer treatment. This is in agreement with the work of Matsuda et al.,[9] who explained this result in terms of enhancement of the CO_2 escape through the pores, which are not totally reduced by sintering at lower temperatures in spite the fact that CO_2 vapor pressure is also lowered.

Refined lattice parameters were found to be $a = 3.817(1)$, $b = 3.883(2)$, $c = 11.672(4)$ Å, space group Pmmm.[10] Assuming the b/a ratio dependence versus oxygen doping,[11] the values correspond to an oxygen-unsaturated $YBa_2Cu_3O_y$ lattice, in particular, to $y \approx 6.7$.

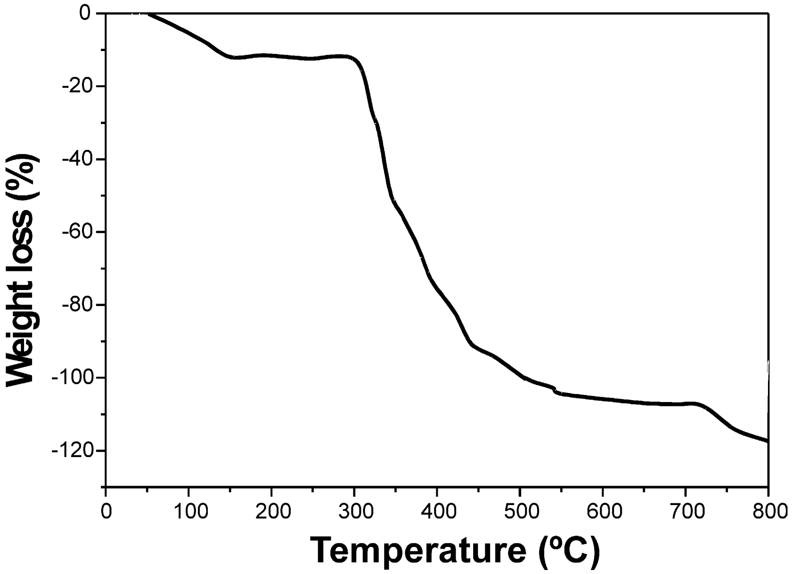

Fig. 2. TGA curve for the calcined Y-123 precursor crust up to 800 °C. Heating ramp: 1 °C/min. Ambient atmosphere: air.

3.2. $La_{2/3}Ca_{1/3}MnO_3$

The composition $La_{1-x}Ca_xMnO_3$ with $x = 1/3$ was chosen since it exhibits the maximum magnetoresistance in the series. These perovskites show the phenomenon of giant magnetoresistance (GMR) and are potential candidates for magnetoelectronics.[12]

Contrarily to Y-123, the magnetoresistive $La_{2/3}Ca_{1/3}MnO_3$ perovskite does not contain low-solubility salts such as $Ba(NO_3)_2$. Therefore, no precipitates were visually observed in this case during foam formation.

The powder XRD pattern is shown in Fig. 5a. Broad and low-intensity reflections signal the amorphous character of the precursor powders. No clear identification has been feasible in that case. The calcined powders at 1000 °C/5 h are shown in Fig. 5b. All reflections correspond to the perovskite phase. It crystallises in the Pbnm space group with refined lattice parameters $a = 5.453(2)$, $b = 5.453(1)$ and $c = 7.709(5)$ Å. These values compare favorably with those early reported by Blasco et al.[13]

Final carbon content was 350 ppm. This low value is consistent with the low basicity of the compound. Again no residual nitrogen is observed in the calcined product.

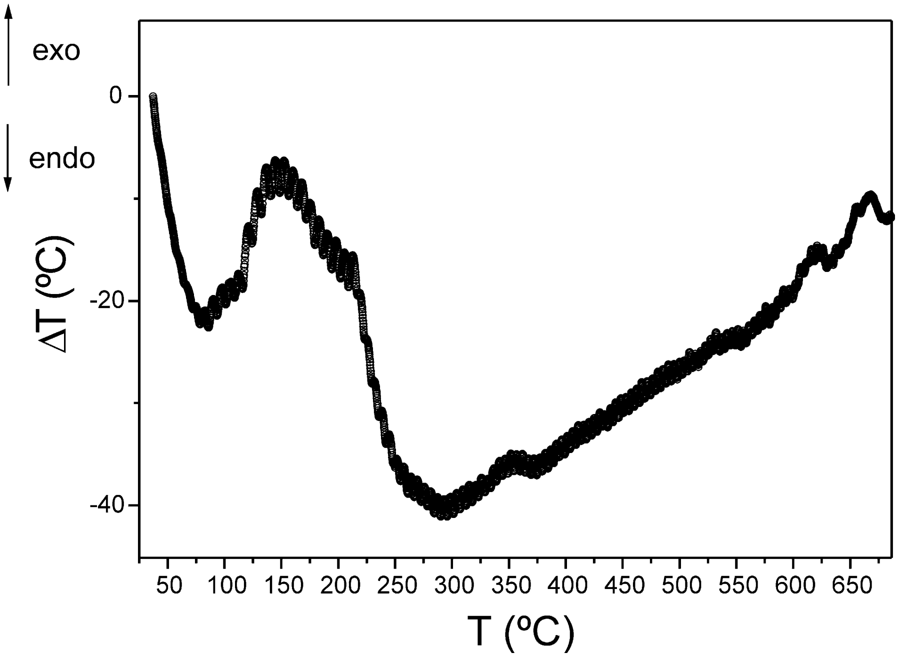

Fig. 3. DTA curve for the calcined Y-123 precursor crust up to 650 °C. Heating ramp: 5 °C/min. Ambient atmosphere: air.

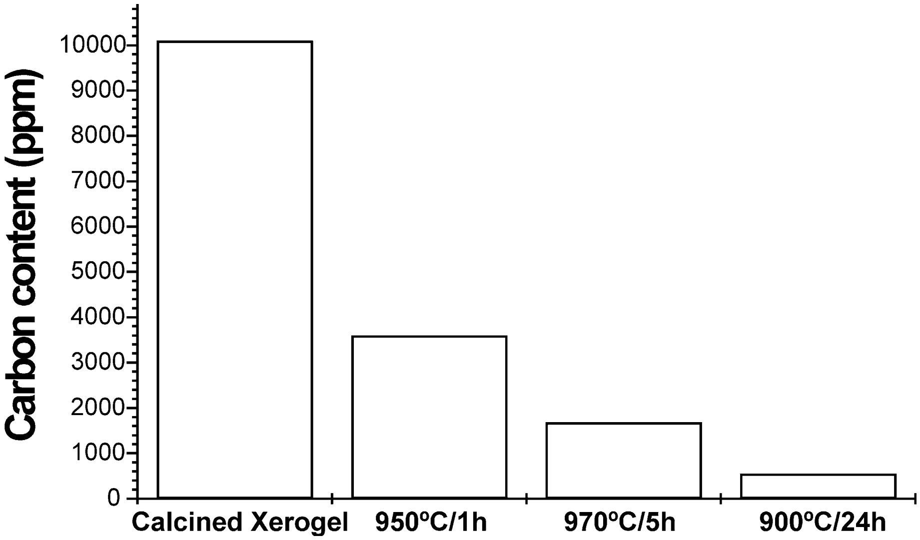

Fig. 4. Carbon content in the calcined powder for different annealing treatments.

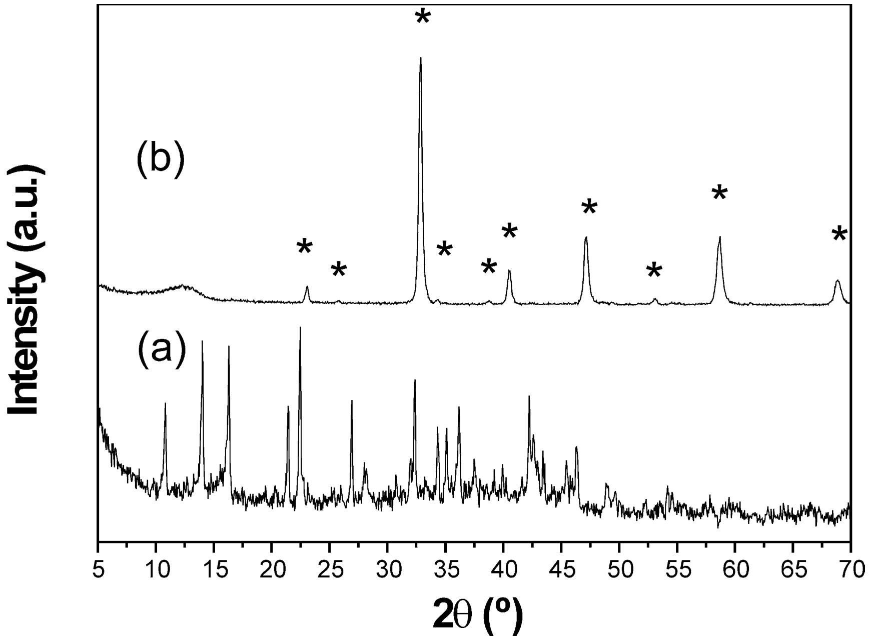

Fig. 5. Powder X-ray diffraction pattern corresponding to the $La_{2/3}Ca_{1/3}MnO_3$ PVA precursor crusts (a) and calcined product at 900 °C/12 h; (b) "*" symbol stands for the perovskite phase. No unambiguous identification could be done with the precursor.

4. Conclusions

The PVA route has been successfully used in the preparation of $YBa_2Cu_3O_{7\text{-d}}$ and $La_{2/3}Ca_{1/3}MnO_3$ electronic ceramic powders in a single calcination step despite the fact that segregation of barium nitrate occurred during solvent evaporation. Carbon content could be reduced below 600 ppm in both cases, which is thought to be a consequence of the porous nature of the gel and the high degree of homogenisation obtained leading to short diffusion paths. Presently, work is being carried out to study the large scale production of powders by the PVA method. Nonetheless, it is anticipated that different processing approaches could be necessary to bring these results to industrial production. Special concerns are the large volume changes during precursor preparation and PVA decomposition control.

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