



The urea combustion method in the preparation of precursors for high- T_C single phase $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ superconductors

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ABSTRACT

An alternative sol–gel route for synthesizing precursors of mercury based superconductors is presented. This route is based on urea as a combustion agent and has been applied in the synthesis of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ (Hg-1223). Moreover, the effects of the precursor preparation on the synthesis of Hg-1223 were studied. This method is further compared with other sol–gel routes used in the synthesis of this family of compounds.

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1. Introduction

The Hg-based superconductors, of general formula $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$, exhibit the highest transition temperatures (T_C) [1,2] among all cuprates. The discovery of superconductivity in this system led to an intense research activity until the present days [3–6]. Their simple tetragonal structure makes this system appealing for the study of the microscopic phenomena responsible for superconductivity [6,7]. Their macroscopic properties have been extensively studied and the discrepancies found on T_C and δ are believed to be related to difficulties in synthesizing pure phase samples [8]. Recent developments on the synthesis processes and in single crystals growth allowed the production of the 1st member of this family, Hg-1201, with high phase purity and in single crystal form [7]. However, for higher members of the series ($n > 2$) the synthesis process is increasingly more difficult and the production of pure phase samples is still complex [8].

The synthesis process of Hg-based superconductors is quite complicated due to the toxicity of Hg compounds and also due to the chemical instability of HgO, used as initial reactant. The decomposition of HgO can be prevented by using encapsulation techniques, such as high pressure [9,10] or synthesis in sealed

ampoules [11,12]. Moreover, these compounds are synthesized in a two step process where, first, a mercury free precursor (mixture of Ba, Ca and Cu oxides) is formed and, secondly, the reaction with mercury oxide (mercuration) is promoted. The mercury free precursor, $\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$, is usually obtained in the form of a mixture of binary and ternary oxides. The precursor, as well the initial oxides, are highly hygroscopic and easily react with CO_2 in air to form carbonate and/or hydroxides of the cations. The reaction of such contaminated precursor with HgO in a closed environment may cause loss of superconductivity and ambiguity in the interpretation of the final properties. Therefore, the high degree of homogenization of the precursor is one of the fundamental factors to obtain high purity superconducting samples [9].

Different methods, such as solid state reaction [9], freeze-drying [13] or sol–gel methods [14,15], have been reported and applied in the synthesis of $\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$ precursors. The sol–gel process appears as an advantageous method since it allows achieving homogeneous mixing of all components at an atomic scale with low processing temperatures and shorter annealing times [14,15]. In addition, this method is a high purity process leading to excellent homogeneity of the final product. Several sol–gel routes have been applied using different complexing agents being the most common ones the acrylamide (AA) [11,15] or organic acids (tartaric and citric) [16]. However, the use of a polymer can easily contaminate the precursor with carbon, limiting the stability of the powders.

In this paper a fast, inexpensive and alternative method to prepare high purity carbonate-free precursors is reported. This process

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has been used to successfully prepare single phase $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ (denoted Hg-1223) samples. Moreover, a comparative analysis with other methods is presented.

2. Experimental

Polycrystalline precursor powders with nominal composition $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_7$ were synthesized using stoichiometric quantities of BaCO_3 (Acros Organic), CaCO_3 (Acros Organic) and CuO (Aldrich). The urea combustion method, widely used to prepare manganites [17], uses this reactant to promote bonding between the metals in solution. The initial reactants were dissolved individually in nitric acid. When the complete dissolution was achieved, all the solutions were mixed and the urea (H_2NCONH_2 , Acros Organic) was added. The amount of urea was fixed at $\psi = 3$, with $\psi = [\text{urea}] / \{[\text{Ba}^{2+}] + [\text{Ca}^{2+}] + [\text{Cu}^{2+}]\}$. The pH was adjusted with addition of ammonia to be in the range where the solution was perfectly clear ($\text{pH} \sim 3$). The solvent was evaporated directly in a hot plate with continuous stirring. Then the temperature started to rise with the exothermic reaction of the urea decomposition. When the temperature reached 463–473 K, the auto-ignition took place. The result was a black powder that was then grounded in an agate mortar. Then, the powder was calcined at 973 K in air with a heating rate of 10 K/min, for 10 h. After, the calcined powder was subjected to two thermal treatments: at 1093 K in air, for 20 h, and the last treatment in dynamic vacuum, for 10 h, with intermediated grindings. To evaluate the influence of the precursor preparation in the synthesis of superconducting Hg-1223 samples, a precursor powder with the same nominal composition, $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_7$, was prepared using acrylamide (AA) as complexing agent. Details on the experimental procedure used in this sol–gel route can be found elsewhere [11,15].

After obtaining the precursors, the mercurations were carried out using the high pressure–high temperature (HP–HT) technique using a Conac type system [18]. The mixture of HgO and the precursor powder was inserted into a gold capsule, suitable for this type of synthesis, which was heated by a graphite furnace. The optimal conditions to obtain superconducting samples were found at 1.8 GPa, 1173 K for 2.5 h.

To evaluate samples' quality, X-ray diffraction (XRD), scanning electron microscopy (SEM) analysis, thermo-gravimetric analysis (TGA) and magnetic measurements have been performed. The XRD measurements were performed using a Siemens D-5000 diffractometer, in transmission mode with $\text{CuK}\alpha$ ($\lambda = 1.54056 \text{ \AA}$) radiation, by step scanning over an angular range between 10° and 90° in increments of 0.05° . The refinement and quantitative analysis of the crystallographic phases was done using Powder cell software [19]. Scanning electron microscopy was carried out using a Phillips microscope, model FEI Quanta 400, at 25 kV. TGA measurements on the precursor powders were performed using a Perkin-Elmer thermo gravimetric apparatus using air as a carrier gas in a rate of 10 K/min.

Magnetic measurements were obtained using a Quantum Design SQUID magnetometer in the range 4–160 K under an applied field of 0.05 T in the zero field cool (ZFC) procedure.

3. Results and discussion

In order to find the optimal synthesis conditions and to explore the effect of the precursor preparation on the production of Hg-1223 superconducting samples, some parameters have been controlled: temperature and atmosphere of the heat treatments. After combustion via auto-ignition, the obtained powders were calcined at 973 K, in air, for 10 h. The same procedure has been applied to the obtained acrylamide xerogel. After calcination, the

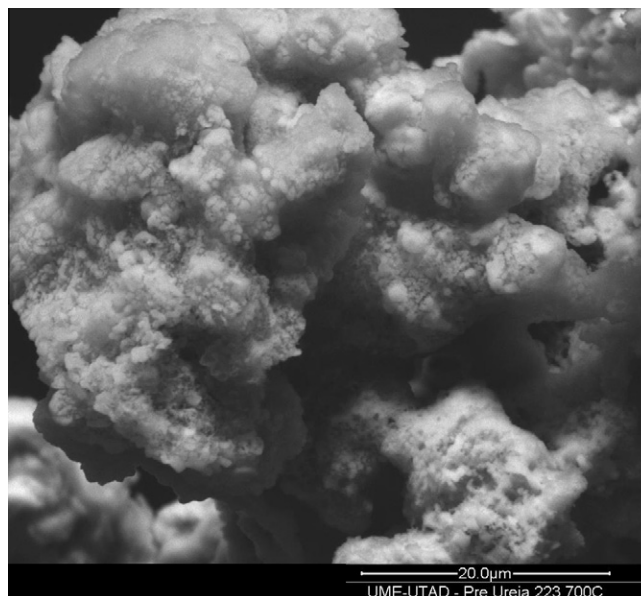


Fig. 1. SEM micrograph of $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ calcined precursor powders obtained via the urea route.

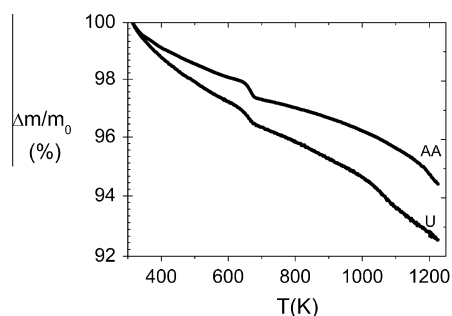


Fig. 2. Thermo-gravimetric curves for the nominal $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ calcined precursor powders obtained via the urea (U) and acrylamide (AA) routes. The measurement was performed in air at a rate of $10^\circ/\text{min}$.

powders presented a mixture of phases including traces of the initial reactants. The urea calcined powders were found to be very thin, as shown in Fig. 1, of the order of $0.5\text{--}1 \mu\text{m}$ though they are agglomerated in aggregates of few μm as observed in precursor powders prepared via the acrylamide method [15].

To control the decomposition mechanisms and determine the synthesis temperatures of the intermediate precursors, thermo-gravimetric (TG) measurements have been performed after the calcination. Fig. 2 shows the TG analysis curves for the $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ calcined powders, obtained via the urea (U) and acrylamide (AA) routes. A weight decrease is observed for both cases being the urea powder more reactive in air with a total weight loss of 8% regarding the 5% loss of the AA powder. A shoulder is observed in the temperature interval 630–680 K, which is probably due to an incomplete nitrate decomposition during the calcination process. Here, the reduction of Cu (II) to Cu (I), which occurs in the same temperature range, is excluded since the measurement was not performed in a reductive atmosphere [20]. After this temperature range, there is a continuous weight loss with a small kink in each curve. For the urea powder, the kink starts at 1000 K while for the AA powder this reaction takes place only at 1180 K. This kink in the curves indicates the start of the carbonates decomposition reactions. This result reveals a better efficiency of the urea in formation of the precursor powders allowing a complete decarbon-

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